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Quinoline Conversion in the Presence of Athabasca Derived Heavy Gas Oil Fractions

by

William S. Kanda (Jr) ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of **Master of Science**

in

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Edmonton, Alberta

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Abstract

Part of processing bitumen from the Athabasca Oil Sands includes hydrotreating, where the coker gas oil distillates are reacted in the presence of hydrogen and catalyst. Hydrotreating removes heteroatoms including nitrogen in a process called hydrodenitrogenation (HDN).

A probe nitrogen compound, quinoline, was used to determine the effects of different weight fractions (cuts) of Athabasca heavy gas oil on quinoline conversion. Quinoline concentration was 1.0 wt% and the reactor feeds varied from 1080 to 3000 ppm nitrogen. The three cuts had boiling ranges of 343-393 °C (light cut), 433-483 °C (intermediate cut), and greater than 524 °C (heavy cut). Reactions were conducted in a 15 mL batch at temperatures of 330, 350, and 380 °C in the presence of a commercially available NiMo catalyst. Typically 30-70 wt% of the quinoline was converted during reaction.

Reactions with different cuts were conducted with constant total nitrogen concentrations, and the heaviest cut was twice as inhibitory than the intermediate cut. The lightest cut also displayed significant inhibition.

The lightest cut deactivated the catalyst by nearly 50 %, while the intermediate and heavy cuts did not appear to deactivate the catalyst.

Concentrated nitrogen extracts from the intermediate and heavy cuts were studied and nitrogen species in the cuts were determined to be important inhibitory compounds.

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Nomenclature

a	Activity
A	Constant in Arrhenius relationship
A_{DHQ}	Gas Chromatography determined area of decahydroquinoline
A_{DMQ}	Gas Chromatography determined area of 2,7-dimethylquinoline
A_Q	Gas Chromatography determined area of quinoline
AR	Gas Chromatography determined ratio of compound of interest's area to internal standard's area
C	Concentration of compound of interest (mol/g)
C_i	Concentration of other compounds (mol/g)
C_o	Initial concentration of compound of interest (mol/g)
C_t	Final concentration of compound of interest (mol/g)
C_{DHQ1}	Concentration of decahydroquinoline after 1st dilution (g/mL)
C_{DHQ2}	Concentration of decahydroquinoline after 2nd dilution (g/mL)
C_{DMQ}	Concentration of 2,7-dimethylquinoline to GC (g/mL)
C_{Q1}	Concentration of quinoline after 1st dilution (g/mL)
C_{Q2}	Concentration of quinoline after 2nd dilution (g/mL)
Cal_{C1}	Gas Chromatography calibration curve proportionality constant (g compound of interest/g internal standard)
Cal_{C2}	Gas Chromatography calibration curve offset constant (g compound of interest/g internal standard)
Ea	Activation energy of reaction (kcal/mol)
$F_{DHQFeed}$	Mass fraction of decahydroquinoline in feed oil
F_{DHQoil}	Mass fraction of decahydroquinoline in product oil
F_{QFeed}	Mass fraction of quinoline in feed oil
F_{Qoil}	Mass fraction of quinoline in product oil
I	Mass fraction of inhbitory compounds (usually cuts)
k	Reaction rate constant (variable units, usually mol Q/g cat/min)
k'	Reaction rate constant before lumping in other constants

k_r	Reaction rate constant with no other constants included
k a	Combined activity and reaction rate constant when examining temperature dependence of k
K	Adsorption constant of compound of interest (quinoline) (g feed / mol Q)
K'	Adsorption constant before other constants included
K_I	Adsorption constant of inhibitors (g feed / g inhibitor)
K'_I	Adsorption constant of inhibitors before other constants included
L	Confidence interval for student-t distribution (95% confidence)
m_{cat}	Mass of catalyst (g)
m_{feed}	Mass of feed (g)
M_{DHQ1}	Mass of decahydroquinoline in 1st dilution (g)
M_{oil}	Mass of oil in 1st dilution (g)
M_{Q1}	Mass of Quinoline in 2nd dilution (g)
MR	Gas Chromatography determined ratio of compound of interest's mass to internal standard's mass
MW_I	Molecular weight of inhibitor (g/mol)
n	Number of replicate reactions in a series
R	Ideal gas constant (3.48×10^{-2} kcal/mol K)
S_o	Number/concentration of available active sites on a catalyst
S_t	Number/concentration of total active sites on a catalyst
t	Time (minutes)
$t_{0.975}$	95% student-t distribution constant
V_L	Volume of liquid feed to reactor (mL)
w_{cat}	Weight of catalyst (g)
W_L	Weight of liquid feed to reactor (mL)
$\bar{X}$	Experimental average of several replicates
ρ_L	Density of feed liquid
σ	Standard deviation of several replicates

1 Introduction

As conventional crude oil resources dwindle, non-conventional oil sources are playing larger roles in meeting the still growing demand for petroleum products. In 1998 over 35 % of Canada's heavy crude supply was from bitumen and that percentage is expected to grow as oil sand production increases and conventional crude supplies increase slowly or hold constant (Kelly, 1999). Kelly (1999) predicts that oil sand production will increase from 140,000 barrels per day (bbls/day) in 1995 to 690,000 bbls/day in 2005, a 495% increase. The 690,000 bbls/day of production will account for 57.5 % of total Canadian production of heavy oil.

Non-conventional oil sources include sources of petroleum from coal oil, tar sands, and oil sands. Non-conventional oil sources introduce a variety of problems, not as common in conventional oil sources, that will have to be solved or improved upon to maximize efficiency and recovery. Problems with extracting the petroleum from the deposit in the ground, separating the valuable resource from the surrounding material, and undesirable and difficult handling and transport properties all are problems that are specific to various non-conventional oil sources and need to be solved or improved upon. Another problem that is common to virtually all non-conventional oils and some conventional oils is the contamination of the oil by various unwanted molecules or class of molecules. Non-conventional oils however tend to have higher concentrations of these unwanted and undesirable molecules.

Heteroatom compounds are one common contaminant of non-conventional oil sources. Heteroatom compounds are compounds that contain atoms other than carbon and hydrogen (i.e. nitrogen, sulfur, or oxygen). Heteroatoms tend to be more concentrated in non-conventional oil sources because the non-conventional oil sources have typically not been located deep underground like conventional oils, but have been accessible to physical, chemical, and biological degradation. For example, Jeong et al. (1994) examined a shale oil that contained 9800 ppm sulfur, 16300 ppm nitrogen. Bej et al. (2001) report on heavy gas oil derived from Athabasca bitumen with a sulfur content of 41000 ppm and a nitrogen content of 3900 ppm. These values are higher than the three oils from conventional sources studied by Shin et al. (2000) which had a sulfur and nitrogen concentration ranging between 4200-9100 ppm and 295-695 ppm, respectively. The heteroatoms are bound in the hydrocarbon molecules, typically as part of a ring structure.

Two classes of nitrogen species exist in oil sources; heterocyclic and non-heterocyclic compounds. Non-heterocyclic compounds are species where the nitrogen atom is not part of a ring structure on a molecule. Amines and nitriles are examples of these types of compounds. Heterocyclic nitrogen compounds have the nitrogen bound in the molecule as part of an otherwise carbon ring structure. Heterocyclic nitrogen compounds have two sub classes, basic and non-basic. Basic compounds like pyridine and quinoline have the free pair of electrons located locally around the nitrogen atom and they are available to participate in acid/base type reactions. Non-basic compounds like indole and carbazole have the free pair of electrons on the nitrogen atom delocalized around the ring structure and they are therefore not available to participate in acid/base type reactions.

Heteroatom removal is most commonly accomplished by hydrotreating. Hydrotreating is the process that reacts the feed oil with hydrogen at high pressures and temperatures over a catalyst. Removal of sulfur and nitrogen is important for several reasons. Sulfur is a serious environmental concern in fuels as it forms SO_2 during combustion. Nitrogen is also somewhat of an environmental concern with NO_x emissions, but the main concern is with the deactivation of downstream refinery catalysts by nitrogen species. Catalytic nitrogen removal, called hydrodenitrogenation (HDN) is one of the reaction processes that occurs during hydrotreating.

HDN of an oil feedstock is typically performed over a NiMo sulfide on alumina catalyst. Generally the non-heterocyclic compounds are the easiest class of nitrogen containing species to undergo HDN. The basic compounds are the next easiest group of nitrogen compounds to remove the nitrogen atom from, and the hardest class of nitrogen species to get to undergo HDN is the non-basic compounds. Bej et al. (2001) found that in Athabasca bitumen derived gas oil, the rate of removal of non-basic compounds was slower than the basic compounds.

Girgis and Gates (1991) suggest that for heterocyclic nitrogen compounds, HDN typically involves the following three steps:

1. The ring structure containing the nitrogen atom is hydrogenated (saturated with hydrogen). Other attached non-nitrogen containing rings may also be hydrogenated.

2. Hydrogenolysis of the carbon-nitrogen bond, which results in breaking of the nitrogen containing ring, giving a primary amine.
3. The nitrogen atom is removed from the broken ring and forms NH_3 and a hydrocarbon molecule without nitrogen.

As higher nitrogen concentration resources are used, more nitrogen removal must be accomplished to ensure increasing nitrogen concentrations do not damage refinery catalysts. Therefore, increasing interest has been generated in understanding HDN processes.

It has long been understood that hydrotreatment products such as H_2S, NH_3, and H_2O can inhibit or accelerate the HDN reactions of various compounds (for example, Satterfield et al., 1985 and Gultekin et al., 1991). Trytten and Gray (1990) found that larger nitrogen species were harder to hydrotreat than the species found in the lighter fractions of Athabasca bitumen coker gas oil. Satterfield et al. (1980), LaVopa and Satterfield (1988a), and others have worked to determine the effects of hydrotreating sulfur and nitrogen species at the same time, as in commercial hydrotreating reactors. Some studies have also been performed with mixtures of different nitrogen species during HDN reactions (Machida et al., 2000). However, little work has been done to identify if other compounds or classes of compounds affect the HDN of nitrogen compounds. It has been hypothesized that higher molecular weight species and polyaromatics can adsorb to the catalyst surface and inhibit the HDN of nitrogen species and even possibly permanently deactivate the catalyst. The high molecular weight nitrogen-containing species may also adsorb to the catalyst surface and inhibit the reaction of lighter molecular weight species. These larger nitrogen compounds may also cause deactivation of the catalyst.

Some work has been done in the above areas, however, more information is required. Jeong et al. (1994) concluded that in coal oil, there was no effect of high molecular weight species on the HDN of indole, however, Liaw et al. (1998) showed that pyridine could inhibit the HDN of aniline.

This work examines the effects of different molecular weight fractions of coker gas oil derived from Athabasca bitumen on the reaction of a probe nitrogen compound. Quinoline (shown in Figure 1.1) was chosen as a model light molecular weight compound in order to observe the effects of the coker gas oil fractions on a lighter nitrogen compound. Using a probe compound in this manner allows for the direct measurement of catalyst inhibition. Using a probe compound allows the activity of the catalyst to be examined separately from the reactivity of the individual gas oil fractions. The deactivation of the catalyst can also be determined separately from the inhibition.

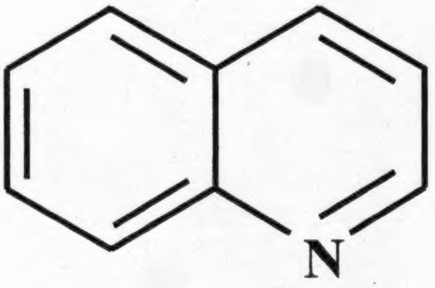


Figure 1.1: Structure of Quinoline

1.1 Objective of Study

The objective of this study was to determine if different fractions of heavy gas oil derived from Athabasca bitumen affected the hydrotreating reactions of a model nitrogen containing compound. Quinoline was used as a model compound and the effects of different gas oil fractions on quinoline conversion were measured in order to determine if the fractions inhibited the quinoline reactions. Nitrogen extracts from the gas oil fractions were used in order to determine if the nitrogen containing species in the gas oil fractions are important in the inhibition displayed or if the inhibition is the result of large polyaromatic (non-nitrogen containing compounds). Using this method identified if any of the gas oil fractions or nitrogen extracts permanently deactivated the hydrotreating catalyst.

This study also examined the effects of a fraction of gas oil on one of the major compounds in the reaction network of quinoline. The effects of the gas oil fraction on the conversion of decahydroquinoline were investigated to determine which reactions of the quinoline HDN pathways the fraction affects.

1.2 Hypothesis of Study

The hypotheses of this work were the following:

1) The presence of nitrogen compounds inhibits the conversion of quinoline.
2) The presence of polyaromatic compounds inhibits the conversion of quinoline.

3) Heavier molecular weight nitrogen compounds will inhibit the conversion of quinoline more than lighter nitrogen compounds.

4) Larger polyaromatic compounds and heavier molecular weight nitrogen compounds (the heavier gas oil fractions) will be the most likely to deactivate the catalyst.

2 Literature Review

As conventional oil reserves slowly dwindle, more and more heavy oils and non-conventional oil sources will be required to meet the continually growing demand for petroleum and petroleum products. Future projections by Kelly (1999) indicated that heavy oil production in Canada, including oil sand bitumen recovery will double between the years 1995 and 2005 to 1.2 million barrels per day. In these predictions the production of bitumen will increase from about 140,000 barrels/day to 690,000 barrels/day, a five fold increase. Heavy oils, and in particular non-conventional oil sources like oil sands, tend to have higher concentrations of undesirable compounds such as covalently bound heteroatoms, which need to be removed from the oil.

2.1 Heteroatom Removal from Oil

Heteroatoms such as sulfur, nitrogen, and oxygen are covalently bound to compounds in the heavy oils. These compounds are undesirable, especially the sulfur and nitrogen species. Sulfur is a concern because of its environmental issues in the formation of SO_2 during combustion as well as for downstream processing issues such as the poisoning of reformer catalysts used for producing high octane gasoline. Angelici (1997) notes that in the year 2000 the US federal regulations required less than 0.04 wt% sulfur and California regulations required less than 0.003 wt% sulfur in gasoline. This is a significant decrease from the pre-2000 limits of 0.1 wt%. The removal of the nitrogen compounds is also important, partially for environmental reasons related to possible increased NO_x emissions on combustion, but primarily due to the poisoning characteristics of nitrogen species on downstream refinery catalysts in hydrocracking and fluid catalytic cracking.

To remove these heteroatoms, the heavy oil is often reacted over a catalyst in the presence of hydrogen gas at high pressures and temperatures in a process called hydrotreating. Hydrotreating is primarily concerned with removing heteroatoms and is not used to break large organic molecules into smaller ones (as in the process of hydroconversion of residue or hydrocracking of gas oil). The process of removing sulfur with hydrogen is called hydrodesulfurization (HDS), the removal of nitrogen is hydrodenitrogenation (HDN), and the removal of oxygen is hydrodeoxigenation (HDO). If there is minimal nitrogen in the heavy oil, and HDS is the only concern in hydrotreating, a CoMo sulfide on alumina catalysts is typically selected. If HDN is a concern the catalyst is usually a NiMo sulfide on alumina catalyst (Angelici, 1997). For a comprehensive review of hydrotreating reactivities, reaction networks, and kinetics see Girgis and Gates (1991).

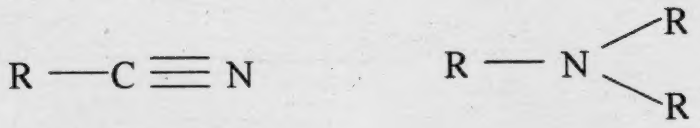
2.2 Nitrogen Removal from Oil

HDN has received somewhat less attention as governmental and environmental regulations have focused on sulfur concentrations. However, as the dependence on non-conventional sources of petroleum increases, HDN is becoming more of a concern for refineries. Non-conventional sources such as coal oils, tar sands, and oil sands tend to be higher in nitrogen compounds than other more conventional heavy oils. According to Jeong et al. (1995), shale oils have much higher nitrogen concentrations than typical crude oils. Girgis and Gates (1991) remark that the removal of nitrogen species has become more of a concern as efforts to convert residua, coal, and shale oil to liquid fuels have increased.

2.2.1 Classification of Nitrogen Compounds

The nitrogen compounds in non-conventional oils are not simple structures, but are a large wide ranging group of compounds that have nitrogen attached. The two major types of nitrogen containing compounds are non-heterocyclic and heterocyclic.

The non-heterocyclic nitrogen compounds are the compounds where the nitrogen atom is not part of an organic ring structure. Examples of this type of nitrogen compound are amines and nitriles. These compounds have the nitrogen atom connected in a non-ring structure type connection. Non-hetrocyclic compounds are usually very quickly removed by HDN processes and are typically not a major concern in nitrogen removal. Figure 2.1 shows the characteristic placement of the nitrogen atom on the organic molecule for both nitriles and amines. Katzer and Sivasubramanian (1979) state that non-hetrocyclic compounds (like pentylamine) are present in petroleum liquids in small amounts, but the low concentration and high reactivity make them of little importance during HDN. Buell (1967) reported that no amines were found in the work with light and heavy gas oil.

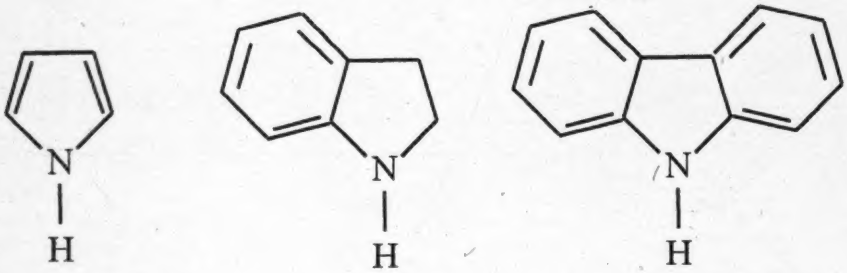


nitrile nitrogen amine nitrogen

Figure 2.1: Non-heterocyclic Nitrogen Compounds

The hetrocyclic nitrogen compounds are compounds where the nitrogen atom is part of a ring structure, including aromatic ring structures. These heterocyclic compounds are further divided into two subclasses, basic and non-basic.

Non-basic heterocyclic nitrogen compounds are the compounds like pyrrole, indole and carbazole where the nitrogen is part of a ring structure, but cannot participate in acid-base type reactions, where H+ protons are accepted (single electrons are donated) by the nitrogen on the ring structure. For these non-basic compounds, the electron pair held by the nitrogen species is delocalized around the ring and are unavailable for donation (as a basic compound does). Non-basic compounds were found to be harder to remove during HDN than basic heterocyclic compounds in Athabasca bitumen derived heavy gas oil (Bej et al., 2001). In the study by Bej et al. (2001), the conversion of non-basic nitrogen compounds was typically 15-35 % lower than the conversion of the basic compounds. Figure 2.2 shows pyrrole, indole, and carbazole, three non-basic nitrogen heterocycles. The compounds shown are non-alkyl substituted, however in petroleum materials alkyl-substituted hetrocycles dominate. Dorbon et al. (1984) report a large number of substituted carbazoles along with unsubstituted carbazole present in coker (heavy) gas oil. Most of the substitutions reported were methyl, dimethyl, or benzo substituted carbazoles.

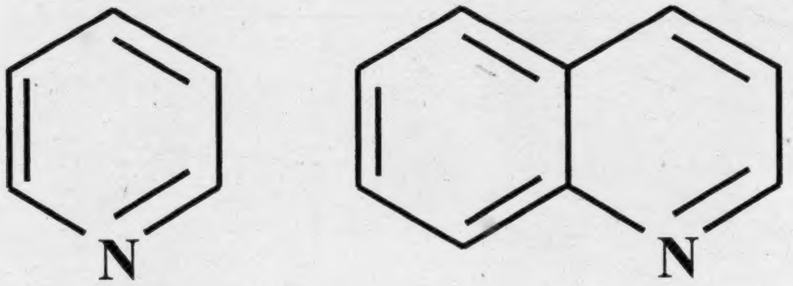


pyrrole indole carbazole

Figure 2.2: Non-basic Heterocyclic Nitrogen Compounds

The basic heterocyclic nitrogen compounds are pyridine, quinoline, and acridine. The nitrogen is part of an aromatic ring as in pyrroles, however, the electron pair is localized at the nitrogen atom and is available to participate in acid-base reactions. Bej et al. (2001) concluded that the basic nitrogen compounds in heavy gas oil derived from Athabasca bitumen are easier to hydrogenate than the non-basic nitrogen compounds. However, any other differences between the basic and non-basic compounds were not examined. Figure 2.3 shows the basic heterocyclic nitrogen compounds of pyridine and quinoline. Although the compounds shown in Figure 2.3 are not substituted, the actual compound that are found in petroleum products are usually alkyl substituted to varying degrees.

McKay et al. (1976) show that the basic nitrogen heterocylic compounds can be much larger than just quinoline. The lighter fractions of the heavy gas oils MaKay et al. examined contained large amounts of substitued pyridine benzologs (pyridine with benzene rings and other (ie. alkyl) substituents attached). Some of the compounds identified had two or three benzene rings attached to the pyridine along with other substituents on the compound like cyclohexane rings.



pyridine quinoline

Figure 2.3: Basic Heterocyclic Nitrogen Compounds

2.2.2 HDN Studies

Bej et al. (2001) examined the heavy gas oil (HGO) derived from the oil sands bitumen by Syncrude Canada Ltd. and found that of the 3900 ppm of total nitrogen in the HGO, 1600 ppm was basic and 2300 ppm was non-basic. In a number of different reactions performed at different pressures, temperatures, hydrogen to oil ratios, and sulfur concentrations, the basic nitrogen compounds were always hydrogenated to a further extent than the non-basic compounds. For example at a reaction temperature of 385 °C, 88 bar, liquid hourly space velocity of

1 h^{-1}, and at a hydrogen gas to HGO ratio of 600 mL/mL, 78.5 % of the basic nitrogen was converted while only 51.1 % of the non-basic nitrogen was converted. Jokuty and Gray (1991) analyzed hydrotreated gas oil from Athabasca bitumen and found the major series of nitrogen compounds extracted from the hydrotreated oil were non-basic alkyl carbazoles substituted with up to 15 carbons. Shin et al. (2000) determined the relative reactivity of nitrogen compounds. Ranked from most reactive to least reactive, they are indole, methylated aniline, methylated indole, quinoline, benzoquinoline, methylated benzoquinoline, carbazole, and then methylated carbazole. From this ranking it can be seen that the basic compounds are more reactive than the non-basic compounds. Also noted is that the side chains also play an important role in the HDN of a given compound, possibly due to steric hindrance affecting the diffusion of the compound into the catalyst pores or to reduce the ability of the compound to adsorb to the catalyst surface.

Although the non-basic compounds are harder to remove, there is still a need to investigate and understand both basic and non-basic HDN in order to reduce the total nitrogen concentration of petroleum products.

2.2.2.1 HDN Mechanisms

A number of good sources explaining the mechanisms of HDN are available such as Prins et al. (1997) and Girgis and Gates (1991). For an in-depth examination of the mechanisms of HDN, reactivities, and kinetics, these references should be consulted. A general description of catalyzed HDN mechanisms is provided below.

The first step is that the nitrogen containing molecule must first diffuse to the catalyst surface (both external bulk liquid diffusion and internal diffusion inside the catalyst pores). The molecule must then attach to the catalyst surface. The hydrotreating catalyst sites are acidic in nature and this helps explain why basic compounds may be easier to hydrotreat. The acid base reactions may aid in compound attachment to the catalyst and may help promote subsequent HDN steps. Once the compound has attached to the catalyst site, the heterocyclic ring must be saturated with hydrogen (a step called hydrogenation). Other rings that are attached to the hetrocyclic ring may also become hydrogenated. Once the heterocyclic ring is hydrogenated (with or without the other rings also being hydrogenated), one of the carbon-nitrogen bonds must be broken, hence breaking the nitrogen containing ring. The carbon-nitrogen bond is broken by replacement with hydrogen (a reaction called hydrogenolysis). The hydrogenation reactions up to the ring breaking step are generally reversible. Consequently, hydrogen may be added to the ring and then subsequently be removed from the ring in a step called dehydrogenation, yielding the original starting compound. A partially hydrogenated reactant may dehydrogenate resulting in a new less hydrogenated product. Once the ring is broken (a generally non-reversible step), the nitrogen atom is no longer part of a ring and can be removed quickly. At or during any one of these steps, the compound may detach from the catalyst, leaving an intermediate compound in the product oil. Once the compound has detached from the catalyst it must diffuse out of the catalyst and then away from the catalyst back to the bulk liquid.

2.2.2.2 HDN Pathway of Quinoline

The simplified HDN reaction network of quinoline is shown in Figure 2.4 as proposed by Satterfield and Yang (1984). The steps up to the ring breaking step are all hydrogenation or dehydrogenation reactions, but once the ring is broken, a large number of different possibilities exist for removing the nitrogen atom and different hydrocarbon products can result. Figure 2.5 shows some of the possible products such as propylbenzene (IX), 1,1-propycyclohexene (VIII), propylcyclohexane (X), and methylpropylcyclopentane (XI). The ring opening of decahydroquinoline (IV) could also yield 3-cyclohexylpropylamine depending on which C-N bond is subjected to hydrogenolysis. This product is reported as an intermediate that was not found during experimentation, possibly because this species would be highly reactive (Satterfield and Yang, 1984). This reaction network (with minor simplifications and/or omissions) is frequently found in the literature. (Prins et al., 1997).

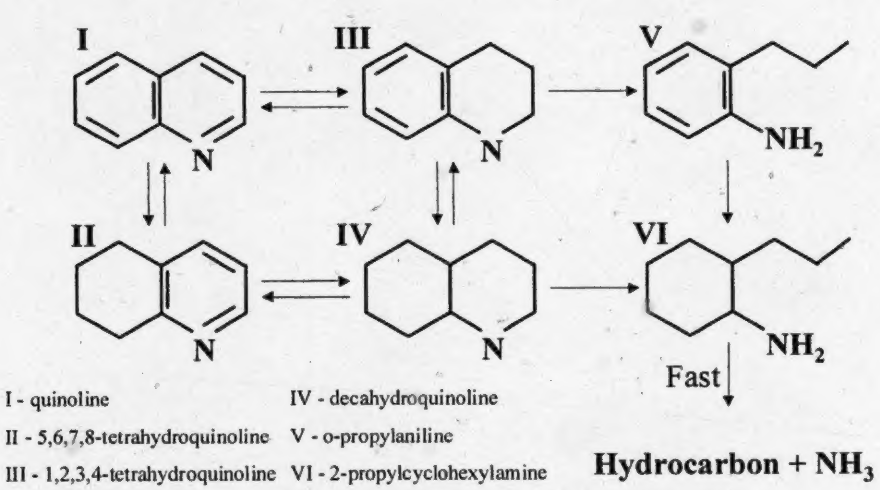

I
III
V
N
N
NH$_2$
II
IV
VI
N
N
NH$_2$
Fast
I - quinoline
II - 5,6,7,8-tetrahydroquinoline
III - 1,2,3,4-tetrahydroquinoline
IV - decahydroquinoline
V - o-propylaniline
VI - 2-propylcyclohexylamine
Hydrocarbon + NH$_3$

Figure 2.4: Simplified Reaction Network for Quinoline (Satterfield and Yang, 1984)

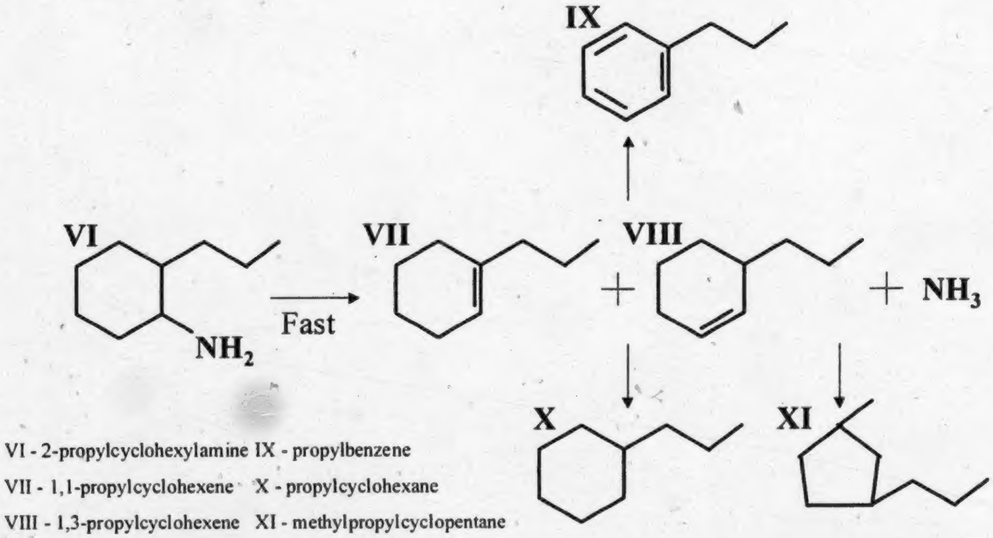

IX
VI
VII
VIII
+
+ NH$_3$
NH$_2$
Fast
X
XI
VI - 2-propylcyclohexylamine
VII - 1,1-propylcyclohexene
VIII - 1,3-propylcyclohexene
IX - propylbenzene
X - propylcyclohexane
XI - methylpropylcyclopentane

Figure 2.5: Hydrocarbon Products from HDN of Quinoline, via propylcyclohexylamine intermediate (after Satterfield and Yang, 1984)

2.2.2.3 HDN Kinetics

Kinetic analysis on HDN and the reaction networks have shown that the reactions can be generally treated with Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expressions (Sundaram et al., 1988, Satterfield and Yang, 1984). Furthermore, for HDN in general and for quinoline specifically, the overall HDN reactions have been found to be 1st order or pseudo first order. Gultekin et al. (1991) in his study of HDN of quinoline found that the reactions were pseudo first order with respect to total nitrogen concentration, where quinoline was the only nitrogen containing species present in the majority of reactions. Rangwala et al. (1990) also reported first order kinetics for nitrogen contents below 0.3 wt% (or less than 3000 ppm total nitrogen). Satterfield and Yang (1984) reported zero order overall HDN reactions for quinoline concentrations over 5 wt% quinoline (or 5400 ppm total nitrogen). The work above studied the kinetics of quinoline in the temperature range of 350 °C to 390 °C.

LHHW kinetics generally have a rate expression in the form of Equation 2.1, where C indicates the concentration of the compound of interest and C_i is the concentration of other intermediates and/or reactants that are absorbed on the catalyst surface. When an inhibitor is present, the rate expression becomes Equation 2.2, where I is the concentration of the inhibitory species.

$$rate = \frac{kC}{1 + KC + \sum_{i=1}^{n} K_i C_i} \qquad \text{Equation 2.1}$$

$$rate = \frac{kC}{1 + KC + K_I C_I} \qquad \text{Equation 2.2}$$

2.3 Reactor Conditions that Affect Hydrotreating

A number of general physical reaction conditions are known to affect hydrotreating reactions, including temperature, pressure, hydrogen partial pressure, and time for reaction.

As temperature increases, the overall HDS, HDN, and HDO rates increase. Girgis and Gates (1991) mention that the increasing temperature causes the thermodynamic equilibrium of hydrogenation reactions to become unfavorable but improves the equilibrium of the carbon-nitrogen hydrogenolysis reactions so even up to 500 °C the overall HDN reactions are favorable. Higher temperatures make the hydrogenation steps less thermodynamically favorable although according to the authors, high hydrogen partial pressures found in industry make the hydrogenation step irreversible.

Also, the reaction rate generally increases as the hydrogen partial pressure and reaction time increase.

2.4 Hydrotreating Catalysts

Commercial hydrotreating catalysts were reported to have used the same formulations for 20 years according to Delmon (1993). The commercially used catalysts are essentially the same as they were in the 1970s (or earlier). Hydrotreating catalysts have typically been a NiMo sulfide on γ-alumina if HDN is desired along with HDS or a CoMo sulfide on γ-alumina if only HDS is required. For a review of hydrotreating catalyst advances and challenges, including new work on supports, promoters, and active metals, the review by Delmon (1993) provides a good starting point.

Typically reported concentrations of Ni, Mo, and promoters tend to be 1-4 wt% for Ni, 5-15 wt% for Mo and 0-6% for promoters. Prins et al. (1997) report that elements P, B, F, and Cl may be used to influence the catalytic performance of the catalyst as well as the catalyst mechanical structure. Liaw et al. (1994) report using a NiMo catalyst with 3.1 wt% Ni and 13.3 wt% Mo with a surface area of 138 m^2/g. Calafat et al. (1996) used a catalyst with a NiMo concentration of 3 wt% and 10 wt% respectively. Eijsbouts et al. (1991) studied a number of NiMo catalysts using phosphorous as a promoter. These authors make the statement that generally Ni is considered to be a promoter for Mo. The work done by these authors used catalysts with a Ni concentration of 1.1-3.5 wt%, a Mo concentration of 6.7-8.1 wt%, and a P concentration of 0-6.2 wt%. Kim and Massoth (2000) report using a catalyst with 3.0 wt% Ni and 16 wt% Mo on alumna support with 2 wt% phosphorous. The surface area of their catalyst was 160 m^2/g. Katzer and Sivasubramanian (1979) show a number of commercially available hydrotreating catalysts and their composition and physical properties.

2.4.1 Initial Coking of Catalysts

When a hydrotreating catalyst is first placed into a reactor for hydrotreating, it must be presulfided in a stable and controlled manner. The catalyst is received fresh in the oxidized state and must be sulfided. Once the catalyst is presulfided and is exposed to feed, a period of rapid deactivation occurs. Once the rapid deactivation is over, the catalyst exhibits an extended period of stability, where a slow and gradual period of deactivation occurs. Absi-Halabi et al. (1991) and Marafi and Stanislaus (1997) examined this rapid initial deactivation of hydrotreating catalysts and show that the rapid deactivation is due primarily to coke formation or carbon deposits on the catalyst surface. Generally the heavier the feedstock the more likely and easily coke is formed on a catalyst surface. The heavier feedstocks have more coke forming ability due to the presence of more polyaromatics.

Heavy metals also tend to foul and deactivate hydrotreating catalysts when they are present in the feedstock. For a comprehensive review of catalyst deactivation, Thakur and Thomas (1985) give a very good review noting catalyst deactivation with various feedstocks, process conditions, and catalyst properties. Furimsky and Amberg (1976) report how a Mo catalyst was poisoned by having benzothiophene adsorb to the surface of the catalyst, blocking the other compounds from reaching the catalyst sites. This type of scenario is reversible poisoning or inhibition of the catalyst as the adsorbed species can be desorbed with the catalyst returning to its previous state.

2.5 General Observations about the Hydrotreating of Compounds

Sulfur and nitrogen are harder to remove from the heavier fractions of oils than from the lighter fractions. The following sections summarize past research in HDS and HDN of distillate fractions.

2.5.1 HDS

Ma et al. (1995) studied the HDS of a gas oil that was fractionated into five separate 20 °C fractions. The gas oil had a boiling range of 227 °C to 377 °C with the five fractions having boiling ranges of <280 °C, 280-300 °C, 300-320 °C, 320-340 °C, and >340 °C, separated by atmospheric distillation. They found the heavier the fraction, the less (slower) the HDS. This result was attributed to three possible reasons. The first reason was that the larger molecular weight sulfur containing compounds were harder to hydrotreat. Ma et al. (1995) report that some heavy compounds were up to 2 to 3 orders of magnitude less reactive than the lighter sulfur containing compounds. The second reason was that other heavy compounds in the heavy fractions inhibited HDS. In particular they suspected that the polyaromatics might inhibit HDS reactions. However, because there was no standard compound to gauge HDS activity, the effects due to lower HDS reactivity in a fraction and the inhibition due to other compounds present in the fraction could not be separated or quantified.

The third reason was that the higher concentration of nitrogen compounds in the heavier fractions was inhibiting HDS. LaVopa and Satterfield (1988a) showed that the presence of quinoline markedly increased the HDS of thiophene at temperatures of 260 °C, but moderately inhibited the thiophene HDS at temperatures of 360 °C. The authors mention that other nitrogen compounds have been shown to inhibit HDS of thiophene over a wide range of temperatures from 250 °C to 400 °C, including one study by Satterfield et al. (1979). Again Ma et al. (1995) could not separate the effect on activity due to this third reason since there was no common compound in all the fractions whose activity could be tracked to determine if inhibition by polyaromatic or nitrogen species was occurring.

Trytten et al. (1990) also found that HDS decreased for heavier fractions of a heavy gas oil (HGO) produced from Athabasca bitumen. Once again lower the reactivity of the heavy sulfur compounds was cited as the reason for the lower HDS, but the relative importance of intrinsic reactivity and inhibition was not determined.

The above work shows that HDS reactions may be inhibited and affected by HDN reactants and products and the presence of large polyaromatic non-heteroatom compounds. Although these results have been well documented and generally accepted for HDS, less work has been done on HDN in this regard. Most work has been directed at identifying compounds that are resistant to HDN, not at identifying compounds or classes of compounds that affect HDN.

2.5.2 HDN

Like the sulfur compounds, the nitrogen species in the heavier gas oil fractions are more resistant to HDN than the nitrogen species in the lighter fractions. Trytten et al. (1990) found that HDN decreased with heavier fractions in Athabasca bitumen derived HGO. Jeong et al. (1995) found that the heavier the fraction of shale oil, the less HDN of the fraction occurred. The lower reactivities of the heavier nitrogen compounds as well as possible diffusion effects and possible inhibition of the catalyst by inhibitory nitrogen species are all cited as possible reasons for the low HDN in heavier fractions, but they could not distinguish between the possible reasons. This type of nitrogen species inhibition was noticed by Machida et al. (2000) when pyridine was found to inhibit the HDN of aniline. These experiments were carried out at 300 °C and a hydrogen partial pressure of 2.29 MPa. The temperature and hydrogen partial pressure used in their experiments are both much lower than typical industrial applications. Machida et al. (2000) determined the adsorption and rate constants of ammonia, aniline, and pyridine and found the reactions followed LHHW predictions. The reaction rate constant for aniline was found to be 4 times larger than pyridine, however, the adsorption constant of pyridine was 18 times larger than for aniline. When a mixture of aniline and pyridine was reacted, the pyridine underwent HDN faster than aniline and acted as an inhibitor to aniline HDN. This work suggested that the presence of a harder to hydrotreat nitrogen compound (pyridine) may inhibit the HDN of another easier to hydrotreat nitrogen compound (aniline). It would be important if this result could be verified using real feeds at conditions closer to actual industrial hydrotreating conditions.

2.5.3 Simultaneous HDS and HDN

Satterfield et al. (1980) reported on the HDN of pyridine and HDS of thiophene performed simultaneously. They showed that the HDS of thiophene inhibited the HDN of pyridine at lower temperatures, but enhanced the HDN at higher temperatures. The temperature at which the inhibition/enhancement crossover occurred was dependent on total pressure. At a pressure of 7.0 MPa, the transition from inhibition to enhancement occurred at 350 °C.

These above results agreed with earlier work by Satterfield et al. (1975) where at temperatures below 325 °C sulfur compounds (thiophene and/or HDS products) reduced the HDN rate of pyridine. The decrease in the reaction rate was attributed to competition between the sulfur compounds and nitrogen compounds for catalyst sites for hydrogenation. At temperatures greater than 325 °C, the carbon-nitrogen bond breaking reactions were thought to be rate limiting, so the presence of H_2S (a C-N bond hydrogenolysis promoter) increased the overall HDN rate.

2.6 Items that Affect HDN

Most of the early work on HDN inhibition was focused on the end products of HDN, HDS, and HDO, namely H_2S, NH_3, and H_2O. The effects of these compounds (either added to the reaction directly or generated in situ) were noted in ideal systems of pure compounds (i.e. quinoline in pure n-hexadecane). As a result, the concentration of products are typically much lower than is typically seen in real industrial hydrotreaters. For example in Satterfield et al. (1985), CS_2 was added to the reactor in a concentration of 8.9×10^{-5} mol/g feed. This corresponds to a sulfur concentration of 0.57 wt% sulfur in the feed which is much less than the typical Athabasca HGO hydrotreater feed of 4.1 wt% sulfur. This suggests that some caution may be needed when applying the findings to real feed/industrial situations.

Satterfield and Gultekin (1981) found that the presence of H_2S in a reactor with quinoline enhanced the HDN of quinoline. The H_2S slightly inhibited the hydrogenation of the rings, but greatly increased the ring breaking reactions (hydrogenolysis). This resulted in a net increase in the HDN rate. Satterfield and Carter (1981) examined the effects of H_2O on the HDN of quinoline. They found that H_2O gave little effect on the HDN of quinoline at 330 °C and 375 °C, but slightly inhibited HDN at 420 °C. They also noted that the presence of H_2O had little effect on the enhancing effects of H_2S shown previously. Satterfield et al. (1985) reported that H_2O did increase the rate of HDN of quinoline. Satterfield and Smith (1986) again reported on the enhancing effects of H_2O. Gultekin et al. (1989) reiterated the enhancing effects of H_2S and H_2O, but also examined the effect of NH_3. They found that NH_3 alone did not affect the HDN of quinoline. However, if NH_3 was present with H_2S, the NH_3 reduced or negated the enhancing effects of the H_2S. This was attributed to the formation of NH_4HS. If the amount of H_2S was increased higher than the NH_3 concentration, the enhancing effects of the H_2S were once again noticed. The studies mentioned above were conducted with pure solvents and much lower heteroatom concentrations than are typically seen in real hydrotreater feedstocks.

2.6.1 Inhibition of Nitrogen Compound HDN by the Presence of Other Species

As mentioned previously, Machida et al. (2000) found that the presence of pyridine can lower the HDN activity of aniline. These results were found using conditions significantly different than typical industrial HDN conditions, however, the results to tend to suggest that harder to hydrotreat nitrogen compounds (pyridine) can inhibit easier to hydrotreat nitrogen species (aniline).

Two other papers reported on the inhibitory action of the heavier compounds on the HDN of lighter nitrogen species. Liaw et al. (1998) hydrotreated different gas oils with different characteristics and properties (primarily type and size of heteroatom compounds). By making blends of different oils, hydrotreating the blend, and then analyzing the product nitrogen species, the authors noted that the HDN of lighter nitrogen compounds found in the gas oils was inhibited by larger nitrogen species. Work done by Jeong et al. (1994) does not support this observation. In the work of these authors, shale oil was fractionated into three fractions (Fraction 1 with a boiling range of 175-275 °C, Fraction 2 with a boiling range of 275-365 °C, and Fraction 3 with a boiling range of 365-455 °C) which were then 'spiked' with indole to act as a model small nitrogen containing compound. These spiked fractions were then reacted and the amount of indole that converted was virtually the same in all three fractions as well as in a blend of the three fractions which would simulate the full (unfractionated) shale oil. The authors report that the amount of indole that reacted was 87.3 +/- 1.8 % in Fraction 1, 86.9 +/- 1.3 % in Fraction 2, 85.2 +/- 1.4 % in Fraction 3, and 85.8 +/- 0.3 % in the mixture of the three fraction. Also, because much more indole reacted in pure hexadecane than in the shale oil fractions, the authors attributed the inhibition of the indole to the competitive adsorption of individual functionalities, in this case nitrogen compounds. These contradictory findings of Liaw et al. (1998) and Jeong et al. (1994) suggest that further study of inhibition effects in hydrotreating is required.

2.7 Summary of Knowledge Gaps

Several studies have shown that the nitrogen removal in heavier gas oil fractions is more difficult than in lighter fractions. However, the lower reactivity of the heavier nitrogen species present in heavier gas oil fractions and the inhibitory effects of polyaromatics and heavy nitrogen species can only be suggested and cannot be singled out in most of the work done so far.

Although some work has been performed in the area of trying to identify if polyaromatics or heavier nitrogen compounds inhibit the HDN of lighter nitrogen species, the answer is still uncertain. The work of Machida et al. (2000) done at conditions significantly different than typical industrial HDN condition seem to support the idea that harder to hydrotreat nitrogen species can inhibit easier to hydrotreat nitrogen species. However, the results of Liaw et al. (1998) and Jeong et al. (1994) performed at more typical industrial HDN conditions with real petroleum feeds seem to contradict each other as to whether higher molecular weight nitrogen or polyaromatic species can inhibit lighter nitrogen species. For these reasons, further investigation into the inhibitory effects of heavier molecular weight compounds on lighter nitrogen species is warranted.

3 Experimental Procedure

3.1 Chemicals

The following chemicals were used in this work:

1) Quinoline from Alfa Products Thiokol/Ventron Division, 99 % Pure.
2) Decahydroquinoline from Aldrich Chemical Company, 97 % Pure mixture of cis and trans isomers.
3) 1,2,3,4-Tetrahydroquinoline from Terochem Laboratories, 97 % Pure.
4) 2,7-Dimethylquinoline from Aldrich Chemical Company, 99 % Pure.
5) Carbon Disulfide from Fisher Chemicals, Certified Grade.
6) Methylene Chloride from Fisher Chemicals, HPLC Grade.
7) Toluene from Fisher Chemicals, Certified ACS Grade.
8) Carrier Gas Oil – a highly hydrotreated light gas oil, 0% S and 25 ppm N concentration. Boiling Range of 213-516 °C, Gray et al. (2000).
9) Nitrogen Gas from Praxair, Prepurified.
10) Hydrogen Gas from Praxair, 6000 psi High Pressure.
11) Never Seez manufactured by Bostik, NSBT-8. (Used on exterior reactor components as a lubricating and anti-seizing compound only).

3.1.1 Hydrotreater Feedstock

Syncrude Canada Limited supplied the samples which were originally derived from Athabasca coker gas oil. All distillations and separations were performed by Syncrude Canada Limited and the samples in this work were used as received.

3.1.1.1 Narrow Boiling Fractions

Syncrude Canada Limited separated a sample of their coker gas oil into narrow boiling fractions, often referred to as 'cuts'. The entire coker gas oil was fractionated into seven different cuts and three of those cuts were used in this work, a light cut (Cut 2), a medium cut (Cut 4), and a heavy cut (Cut 8). Table 3.1 shows the boiling range of the cuts as well as the elemental analysis. Table 3.2 shows some of the selected physical properties for the different cuts.

Table 3.1: Coker Gas Oil Narrow Fraction Boiling Range and Elemental Analysis (Adjaye, 2001)

Cut #	Boiling Range (°C)	wt% of Feed	Mol Wt.	S (ppm)	N (ppm)	C (wt%)	H (wt%)
Whole Feed	Feed			40740	3960		
Cut 1	IBP/343	19.2		38230	1737	85.1	11.08
Cut 2	**343/393**	**19.1**	**266**	**38640**	**2412**	**85.4**	**10.72**
Cut 3	393/433	18.0	318	39320	3244	85.1	10.69
Cut 4	**433/483**	**21.2**	**362**	**41330**	**4203**	**85.1**	**10.50**
Cut 6	483/504	5.6	404	43790	5228	85.0	9.76
Cut 7	504/524	6.4	470	44860	5739	85.1	9.49
Cut 8	**>524**	**9.1**	**590**	**46100**	**6804**	**85.2**	**9.25**

Table 3.2: Coker Gas Oil Narrow Fraction Physical Properties (Adjaye, 2001)

Cut #	Boiling Range (°C)	wt% of Feed	Asphaltenes (%-in Pentane)	MCR (%)	Ext Mat (% Res)	Total Acid Number	^{13}NMR % Aromatic Carbon
Whole Feed	Feed		1.55	1.98	0.003		38.12
Cut 1	IBP/343	19.2	0.02	0.07		0.7	32.59
Cut 2	**343/393**	**19.1**	**0.10**	**0.07**		**2.1**	**34.25**
Cut 3	393/433	18.0	0.18	0.23		2.6	34.51
Cut 4	**433/483**	**21.2**	**0.20**	**1.18**		**2.5**	**35.89**
Cut 6	483/504	5.6	0.16	2.35	0.3	2.4	38.61
Cut 7	504/524	6.4	0.18	5.29	0.27	2.0	41.67
Cut 8	**>524**	**9.1**	**12.67**	**19.12**	**0.80**	**1.9**	**43.05**

3.1.1.2 Nitrogen Extracts

Syncrude Canada Limited separated some of the above cuts further in order to concentrate the nitrogen species present in the cut. The extracts were prepared by column chromatography, in a method similar to the one found in Jokuty and Gray (1991). The column retained the nitrogen containing compounds and then stronger solvents eluted the compounds. The two stronger solvents used were methanol and methylene chloride. The extracts in the methylene chloride phase would likely be less polar, and the extracts in the methanol phase would likely be more polar. Only the extracts from two cuts were examined during this study. Table 3.3 shows the elemental analysis on the Cut 4 and Cut 8 nitrogen extracts. The nitrogen extracts were to be used in order to determine if the nitrogen species in the cuts were important inhibition or deactivation compounds or if the non-nitrogen containing species played a major role in the inhibition and/or deactivation.

Table 3.3: Coker Gas Oil Narrow Fraction Extract Elemental Analysis (Nowlan, 2001)

Cut #	Extract	wt% of Cut	S (ppm)	N (ppm)	C (wt%)	H (wt%)
Cut 4 Whole	Whole	100	41330	4203	85.1	10.50
Cut 4	CH_2Cl_2	16.0	65730	12460	83.6	7.3
Cut 4	CH_3OH	3.2	29460	31300	79.9	8.8
Cut 8 Whole	Whole	100	46100	6804	85.2	9.25
Cut 8	CH_2Cl_2	23.9	53560	8630	82.9	8.2
Cut 8	CH_3OH	3.9	39810	21830	79.3	8.7

3.1.2 Catalyst

The catalyst used in this study was obtained from Syncrude Canada Limited. The catalyst was a commercially available Ni-Mo hydrotreating catalyst. From the manufacturers data sheet, the catalyst contained 12-20% Mo and 2-4% Ni by weight on γ-alumina. The pore volume was in the range of 0.4-0.8 mL/g and surface area in the range of 160-250 m^2/g. The catalyst was a tri-lobe catalyst and had been previously used for a hydrotreating study in a pilot plant reactor (Yui and Ng, 1995). Previously used catalyst was chosen for this study so the catalyst would already be sulfided and coked, and not subject to the initial period of rapid deactivation that occurs with fresh catalyst (Absi-Halabi et al., 1991 and Marafi and Stanislaus, 1997). Any inhibition or deactivation noticed during this study would then likely be due to the feedstock and not due to the normal deactivation of the fresh catalyst.

The catalyst was received mixed with silicon carbide. The silicon carbide had been used during the Syncrude hydrotreating study as volume filler with the catalyst pellets interspersed in the mixture. The catalyst was separated from the silicon carbide by mechanical separation. Most of the silicon carbide was removed by rubbing the catalyst between gloved fingers. Additional silicon carbide was removed by heating the catalyst in an oven for short periods of time (2-4 minutes at a time at 70-80 °C). This heating made the layer of hydrocarbon coating the pellets (residual oil from the previous study) less viscous with lower surface tension and the remaining silicon carbide could be removed more effectively. The catalyst was heated in the oven in this fashion 3 to 5 time depending on the amount of silicon carbide remaining after each cleaning attempt.

3.2 Experimental Equipment

The following sections describe the equipment used during this work.

3.2.1 Micro Batch Reactor

A schematic of the micro batch reactors used in this work is shown in Figure 3.1. The closed and sealed reactor is in Figure 3.1, while the reactor is separated into the four components of the reactor (bottom, tube, top, and valve tubing) in Figure 3.2. This microreactor design had been used previously at the University of Alberta for coking experiments (Tanabe and Gray, 1997) and residue hydroconversion experiments (Richardson and Gray, 1997), however this was the first study to use these reactors for hydrotreating processes. The reactors consisted of a 6.8 cm, 3/8" stainless steel tube with a Swagelok stainless steel fitting on each end. The bottom fitting was a simple cap in order to seal the bottom of the reactor.

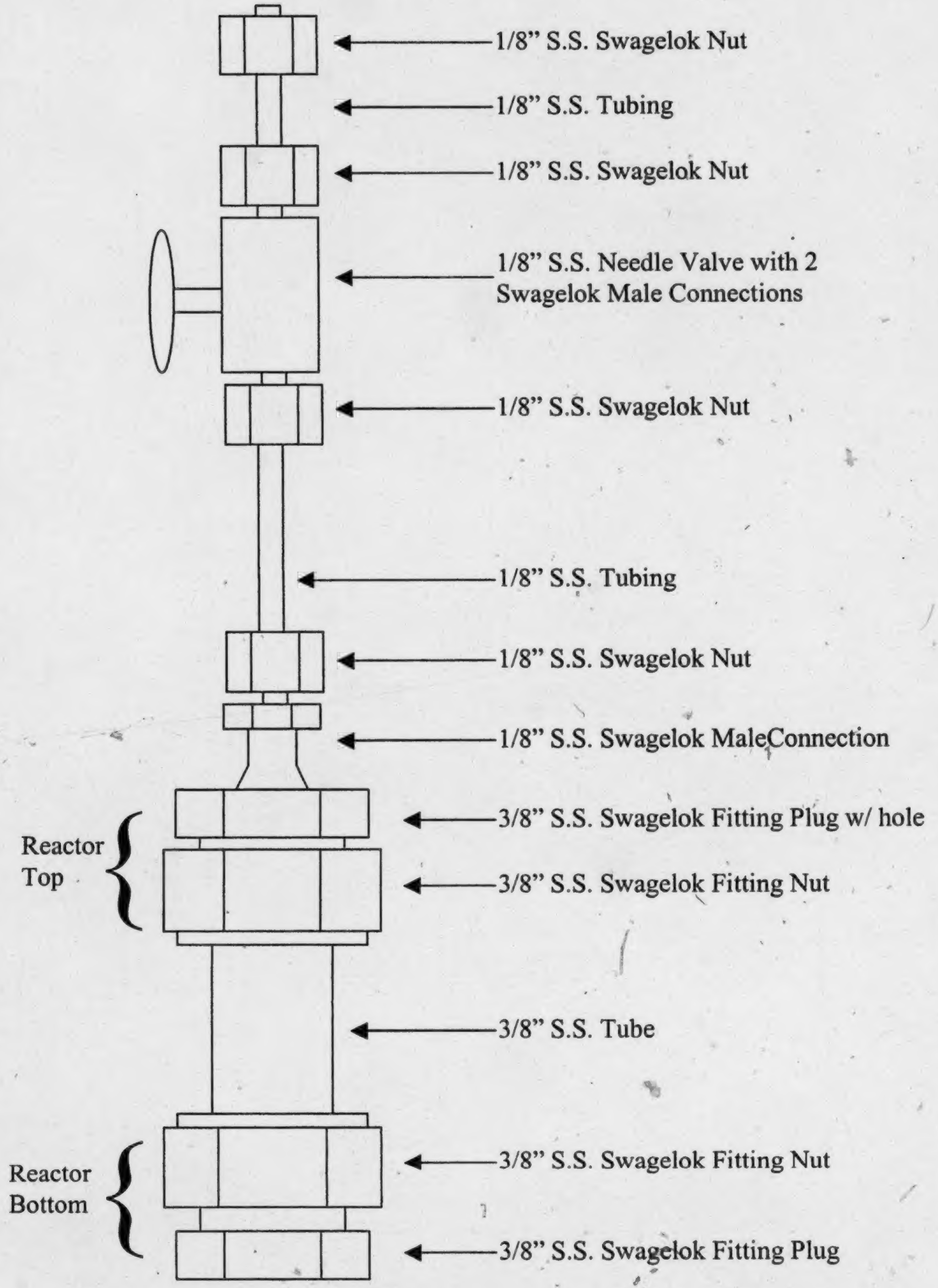

1/8" S.S. Swagelok Nut
1/8" S.S. Tubing
1/8" S.S. Swagelok Nut
1/8" S.S. Needle Valve with 2 Swagelok Male Connections
1/8" S.S. Swagelok Nut
1/8" S.S. Tubing
1/8" S.S. Swagelok Nut
1/8" S.S. Swagelok MaleConnection
3/8" S.S. Swagelok Fitting Plug w/ hole
Reactor Top
3/8" S.S. Swagelok Fitting Nut
3/8" S.S. Tube
Reactor Bottom
3/8" S.S. Swagelok Fitting Nut
3/8" S.S. Swagelok Fitting Plug

Figure 3.1: Schematic of Closed Microreactor

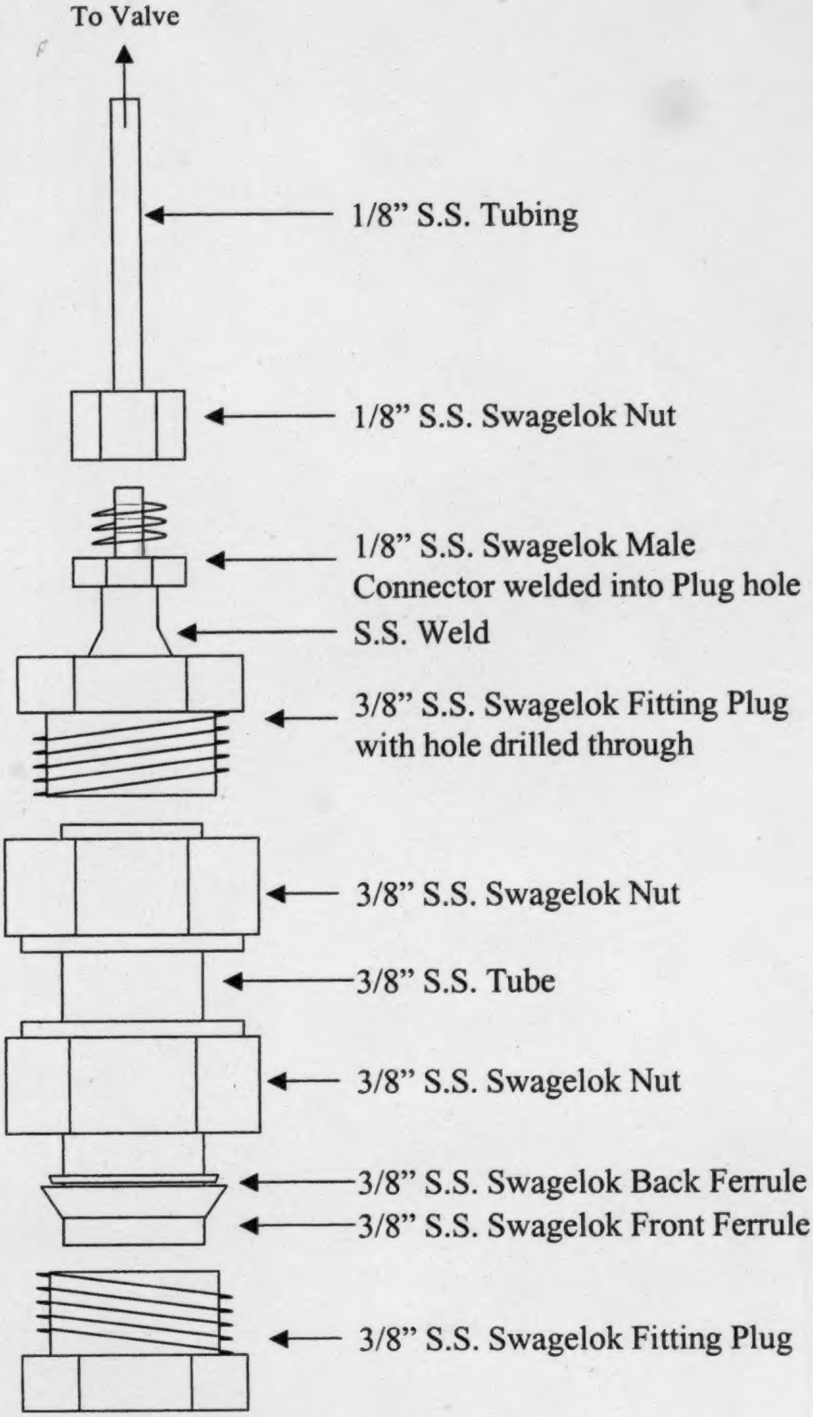

To Valve
1/8" S.S. Tubing
1/8" S.S. Swagelok Nut
1/8" S.S. Swagelok Male Connector welded into Plug hole
S.S. Weld
3/8" S.S. Swagelok Fitting Plug with hole drilled through
3/8" S.S. Swagelok Nut
3/8" S.S. Tube
3/8" S.S. Swagelok Nut
3/8" S.S. Swagelok Back Ferrule
3/8" S.S. Swagelok Front Ferrule
3/8" S.S. Swagelok Fitting Plug

Figure 3.2: Schematic of Separated Microreactor

The top fitting was a cap that had a hole drilled through it and a 1/8” male Swagelok fitting welded into the hole. This connection was where the purge, reactant, and product gases were filled or emptied from the reactor. Attached to the 1/8” male connector was approximately 15 cm of 1/8” stainless steel tubing with a high pressure stainless steel needle valve attached at the other end with Swagelok fittings. A 2-4 cm length of 1/8"”stainless steel tubing connected to the male connector on the valve had a 1/8” female connector that was used to connect the reactor to the hydrogen gas cylinder.

Since the use of the reactors required the opening of the 3/8” fittings after each reaction, eventually the reusable seal provided by the fitting ferrules in the Swagelok connectors became damaged. Either the reactor would no longer seal during pressure testing or the Swagelok connections would deform the tube to the extent that the connectors could no longer be removed from the tube and the reactor could not be opened easily. Difficulty opening the reactors was magnified with the added space and mobility restrictions required with the use of a glove bag, since the reactors could not be opened outside of the glove bag with the risk of exposing the catalyst to the air. Once the reactors were no longer sealing or opening acceptably, they were removed from service and replaced. The reactors typically required replacement every 10 to 30 reactions. All of the reactors were built by the University of Alberta Chemical Engineering Department Machine Shop and were constructed using similar materials, measurements, and methods.

3.2.2 Sand Bath

The sand bath used during this work was a Tecam Fluidized Sand Bath Model # SBS-4. A picture of the sand bath is shown in Figure 3.3. The sand bath was filled with approximately 20 cm of silica sand. Air was sparged into the sand bath near the bottom of the sand level through a distributor. Air was used to fluidize the sand in the sand bath to increase the rate of heat transfer from the heating element to the sand and then from the sand to the reactor. The flow of air to the sand bath was throttled by a needle valve and the flow rate was set at 60 % of scale on a Gilmont D1703 rotameter. This constant air flow setting ensured that the heat transfer rate remained constant throughout this work.

The temperature of the sand was recorded by a thermocouple mounted in the sand 8 cm above the air distributor. An OMRON E5CK model controller, using the thermocouple in the sand as a sensor controlled the temperature of the sand. The heating element was controlled in an on/off fashion by the controller, resulting in a steady state sand bath temperature that had a periodic fluctuation.

An off-center cam was attached to a motor mounted above the sand bath. Reactors were attached to a rod and when they were immersed in the sand bath, the upper arm of the rod was placed on the cam and the motor was switched on. This caused the reactor to be raised and lowered in the sand bath, causing mixing inside of the reactor. The reactor was raised and lowered a total of 3 cm at a frequency of 3 Hz

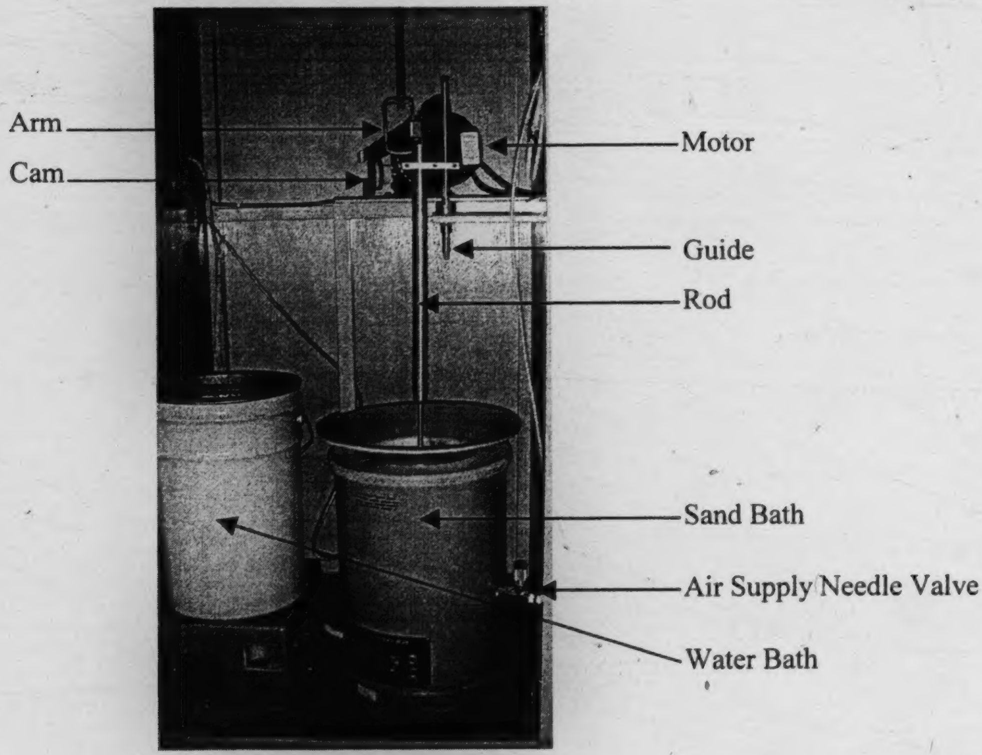

Arm
Cam
Motor
Guide
Rod
Sand Bath
Air Supply Needle Valve
Water Bath

Figure 3.3: Picture of Sand Bath Setup

3.2.3 Glove Bag

The glove bags used during this work were made by Instruments for Research and Industry from Cheltenham, PA. The bags were obtained from Labcor in Anjou, QC. Early work used a 97 cm by 97 cm (37 inch by 37 inch) glove bag model X37-37 while the majority of the work was performed inside of a smaller 69 cm by 43 cm (27 inch by 17 inch) glove bag model X27-17.

The glove bags were connected to the N_2 cylinder via a combination of plastic and metal tubing and a needle valve was used to fill the bag and stop the N_2 flow.

Because the catalyst is active in the sulfided state, and exposure to oxygen could affect the short and long term activity of the catalyst, catalyst exposure to oxygen was minimized by only exposing the catalyst to the low oxygen atmosphere inside of the glove bag.

3.2.4 Gas Chromatograph

The analysis of the feed and product samples was performed with an HP 5890 GC with an autosampler. The GC had an HP-1, Crosslinked Methyl Silicone Gum column. The column ID was 0.32 mm and was about 25 m long and had a film thickness of 0.17 μm. After the preliminary validation work, concern about the possibility of depositing heavy compounds from the cuts and extracts in the front end of the column prompted the installation of 1m of non-polar fused silica 0.32 mm ID column for use as a guard column. The guard column would sacrificially capture heavy component deposits and then could be cut off if problems developed, without shortening the active column. No column plugging issues arose during this work. The detector was a Flame Ionizing Detector (FID) operated at a temperature of 320 °C.

The gas flows to the GC were measured and are shown in Table 3.4. These flows were recorded when the GC column, inlet, and detector temperatures were

30 °C. The helium gas was left running the entire time and the other gas flows were calculated by taking the total flow rate and subtracting the helium flow rate. The amount of air was not recorded for the split or purge vent lines. The gas flows were not checked or measured often, instead, frequent calibrations of quinoline standards were used to ensure GC accuracy and reliability.

Table 3.4: GC Gas Flow Rates

Location	He (mL/min)	H_2 (mL/min)	Air (mL/min)
Split Vent	3.6	0	NR
Purge Vent	2.4	0	NR
Detector	20.0	247	38.8

The GC temperature program used for quinoline analysis is shown in Table 3.5. The GC temperature program used for the decahydroquinoline (DHQ) analysis is also shown in Table 3.5. The major difference between the two different methods was the higher inlet temperature of 300 °C for quinoline instead of 230 °C for DHQ. It was found that the higher inlet temperatures resulted in very small DHQ peaks, and as the inlet temperature was lowered, the peaks became larger and more repeatable. It is believed that the higher inlet temperature was serving to decompose the DHQ and the solvent peak was hiding the decomposition products.

Table 3.5: GC Temperature Program Operation

Parameter	Temperature Program	
	For Quinoline Analysis	For Decahydro-quinoline Analysis
Sample Volume	1 stop (1 μL)	1 stop (1 μL)
Inlet Temperature	300 °C	230 °C
Detector Temperature	320 °C	320 °C
Initial Purge Valve	Off	Off
Purge Valve On Time	1.0 min	1.0 min
Initial Oven Temperature	40 °C	40 °C
1st Temperature Ramp	10 °C/min to 80 °C	10 °C/min to 80 °C
1st Plateau Hold Time	0.0 min	0.0 min
2nd Temperature Ramp	1.5 °C/min to 120 °C	1.5 °C/min to 120 °C
2nd Plateau Hold Time	0.0 min	0.0 min
3rd Temperature Ramp	20 °C/min to 270 °C	20 °C/min to 270 °C
3rd Plateau Hold Time	30 min	30 min

3.3 Reaction Procedure

The following section details the reaction procedures used during this work.

3.3.1 Reactor Feed

Quinoline was chosen to act as a model basic nitrogen compound in this study because it had a good reactivity, was readily available, and was easily quantifiable using an available Gas Chromatograph (GC). Quinoline was also considered to be a relatively non-volatile, stable compound which would aid in quantification during this project.

The feed to the reactor was prepared in one of the following two ways.

For feed with no coker gas oil cuts or extracts (called clean feed), and blends with Cut 2, Cut 4, and the Cut 4 nitrogen extract feeds, the quinoline, carrier gas oil, and cut or extract (if applicable) were mixed together in the required proportions.

With the exception of the Cut 4 methanol nitrogen extract, the feed mixtures all blended together to form a visually homogenous liquid mixture. The methanol nitrogen extract did not dissolve or blend in with the mixture well, but remained a solid suspended in a liquid. A more detailed discussion on the Cut 4 methanol extract mixture is found in Section 4.6.1.2.

For the Cut 8 and Cut 8 nitrogen extracts, the feeds were prepared by first mixing together the required amount of quinoline and carrier gas oil. Since the cut and extracts were solid at room temperature, they were not mixed into the quinoline and carrier gas oil. Instead, weighed amounts were added to the reactor directly as a solid, then the blend of liquid quinoline and carrier gas oil was added. The agitation of the reactor and the relatively long reaction times ensured that the Cut 8 would blend effectively into the liquid. The product oil after reaction with Cut 8 and Cut 8 nitrogen extracts always appeared to be a homogenous liquid (no solids or 2-phase liquids), suggesting the Cut 8 dissolved into the liquid phase upon heating.

The general sequence of the feeds to the reactors was to start a new batch of catalyst with clean feed in order to determine the baseline clean feed activity and then to add one of the feeds containing coker gas oil fractions to determine the inhibition of an individual cut. Clean feed was then fed to the reactor to determine the extent, if any, of deactivation. If deactivation was not noticed, the next cut would be reacted with the same catalyst batch. Cut 4 was used most frequently and usually first, to serve as a benchmark for the catalyst activity with a cut present.

3.3.1.1 Experiments with 3000 ppm total Nitrogen Feed

The experiments with 3000 ppm total nitrogen feed used a constant amount of quinoline in the feed and adjusted the amount of coker gas oil cut mixed in with the feed to bring the total amount of nitrogen present in the feed mixture to 3000 ppm nitrogen. The baseline feed mixture to the reactor, that did not have any cut present, was called clean feed and consisted of 1 % by mass of quinoline in the feed, resulting in a total nitrogen concentration of 1110 ppm, including the 25 ppm nitrogen in the carrier gas oil. When Cut 2, Cut 4, Cut 8, or a nitrogen extract feed was to be fed to the reactor, the concentration of quinoline was held constant and enough cut or extract was added to provide a total nitrogen concentration of 3000 ppm N. This method ensured that the amount of quinoline present in the reactor was always constant, with varying amounts of cut or extract keeping the same total nitrogen concentration. Table 3.6 shows the various feeds that were used during the work involving 3000 ppm total nitrogen. The amount of sulfur in the feed is shown prior to the CS_2 addition.

Table 3.6: 3000 ppm Total Nitrogen Feeds

Feed	Quinoline (wt %)	Cut/Extract (wt%)	Carrier Gas Oil (wt%)	N in Feed (ppm)	S in Feed (ppm)
Clean	1	0	99	1110	0
Cut 2	1	79.4	19.6	3005	30683
Cut 4	1	45.6	53.4	3013	18834
Cut 8	1	28.1	70.9	3017	12977
Cut 4 CH_2Cl_2 Extract	1	15.4	83.6	3021	10104
Cut 4 CH_3OH Extract	1	6.1	92.9	3023	1803
Cut 8 CH_2Cl_2 Extract	1	22.2	76.8	3019	11887
Cut 8 CH_3OH Extract	1	8.8	90.2	3023	3493

3.3.1.2 Experiments with 2000 ppm total Nitrogen Feed

The 2000 ppm nitrogen study feeds were blended in a similar fashion as the 3000 ppm total nitrogen feed study. The clean feed reactions once again had 1 % by weight quinoline for a total nitrogen concentration of 1110 ppm. For this piece of the study, only half as much of the coker gas oil cuts were added so that the total nitrogen concentration was raised to around 2000 ppm instead of 3000 ppm. No extracts were studied at this total nitrogen concentration. Table 3.7 shows the various feeds that were used during the 2000 ppm total nitrogen portion of this study.

Table 3.7: 2000 ppm Total Nitrogen Feeds

Feed	Quinoline (wt %)	Cut/Extract (wt%)	Carrier Gas Oil (wt%)	N in Feed (ppm)	S in Feed (ppm)
Clean	1	0	99	1110	0
Cut 2	1	39.7	59.3	2057	15342
Cut 4	1	22.8	76.2	2061	9417
Cut 8	1	14.1	84.9	2064	6489

3.3.1.3 Varying Quinoline Concentration

In order to obtain kinetic information on the rate of quinoline reaction, the quinoline concentration was varied during one of the reaction series. No cut or extract was used, but the concentration of quinoline in the reactor varied from 0.5 % to 3.0 % by weight. Table 3.8 shows the various feeds used which had varying quinoline concentrations.

Table 3.8: Varied Quinoline Concentration Feeds

Feed (nominal title)	Quinoline (wt %)	Carrier Gas Oil (wt%)	N in Feed (ppm)	S in Feed (ppm)
500 ppm	0.50	99.5	567	0
1000 ppm	1.00	99.0	1110	0
1500 ppm	1.50	98.5	1652	0
2000 ppm	1.98	98.02	2172	0
3000 ppm	2.74	97.26	2996	0

3.3.1.4 Quinoline Intermediates - Decahydroquinoline

A very limited number of experiments (one series) were performed with decahydroquinoline (DHQ). These experiments were intended to help identify the particular reaction steps that were being inhibited or deactivated by the cuts and extracts, i.e. the hydrogenation reactions or the ring cracking hydrogenolysis reactions or both. A summary of these DHQ feeds is shown in Table 3.9.

Table 3.9: Decahydroquinoline Feeds

Feed	Decahydroquinoline (wt %)	Cut/Extract (wt%)	Carrier Gas Oil (wt%)	N in Feed (ppm)	S in Feed (ppm)
Clean	1	0	99	1030	0
Cut 8	1	28.1	70.9	2940	12954

3.3.2 Catalyst Presulfidation

The catalyst was separated from the silicon carbide that it was mixed with when it was received from Syncrude Canada Limited. Because the catalyst had been exposed to air and other unknown conditions, it was decided to sulfide the catalyst before using it in this work. Batches of catalyst were sulfided by loading the catalyst in the micro batch reactor with 140 μL of CS_2 per gram catalyst

(140 μL/g cat). The reactor was then pressurized with 900 kPa of H_2 (at room temperature) and then placed in the sand bath at 350 °C for 2 hours. After the reactor was removed from the sand bath, it was quenched in a water bath and then the product gas purged. The reactor was then re-pressurized with H_2 and then purged again to lower the concentration of H_2S potentially in the reactor. The reactor was then opened in the glove bag and the catalyst removed from the reactor. The catalyst was then sealed in a vial and the vial was sealed inside of a glass jar. The sulfided catalyst was placed in a freezer until subsamples of catalyst were selected from the larger sulfided catalyst batch for use in this work.

Subsamples of catalyst from the larger presulfided batch of catalyst consisted of 0.140 to 0.150 g of catalyst and comprised of 10-13 whole catalyst pellets usually between 3 and 8 mm long.

3.3.3 Reactor Loading

The feed was weighed into the reactor by placing the reactor with the bottom cap fully tightened and an open top on a scale and then pipetting the feed into the reactor until the correct amount had been added. With the Cut 8 and Cut 8 nitrogen extract feeds, the solid Cut 8 or extract was removed from a freezer and then scooped into the reactor on the scale. After adding the correct amount of the solid, the oil/quinoline mixture was then added. This resulted in the amount of feed added to the reactor usually being +/- 0.007 g the amount desired due to over/under shooting of the targeted amount of feed.

After the feed was placed in the reactor, the reactor and the reactor top were placed inside of the glove bag. The catalyst batch to be used was in the glove bag, either inside of the vial/jar assembly if it was the first reaction of the day for that catalyst batch, or inside of a freshly reacted reactor. CS_2 in a vial and a 50 μL syringe were also placed inside of the glove bag.

The glove bag was then almost completely sealed and the nitrogen flow to the bag was started. The bag was allowed to inflate and then external pressure was applied (by leaning on the bag) causing the bag to deflate. This inflate/deflate cycle was repeated two or three times and then the bag closure was completely sealed and the bag was inflated for a final time to the working volume. This repeated inflation/deflation cycle was used to minimize the amount of oxygen present inside of the glove bag.

The catalyst was removed from the vial/jar or the reactor and then placed inside of the reactor containing the feed. A more detailed explanation of the removal of the catalyst is given later in Section 3.3.6. An aliquot of 30 μL of CS_2 was then put into the reactor with the syringe. The reactor was then closed inside of the glove bag by placing the top fitting of the reactor together and tightening the fittings to finger tightness. Although this would not seal the reactor, it would limit the amount of air that would enter the reactor when it was removed from the glove bag for final sealing.

3.3.4 Reactor Sealing

Once the reactor top had been tightened in the glove bag, the glove bag was opened and the reactor was removed. The top of the reactor was then loosened slightly (but not opened) and Never Seez was applied to the threads of the reactor top. Never Seez made the Swagelok fittings thread together better and usually resulted in a better reactor seal, preventing leaks during reaction. Also, the anti-seizing properties of the Never Seez made the reactor easier to open after reaction. The reactor was then placed in a bench vise and the top of the reactor was tightened with a wrench to seal the reactor.

After the reactor top was tightened, the reactor was connected to the H_2 cylinder with the valve set up shown in Figure 3.4, and pressurized by opening the H_2 cylinder valve (Valve #1), H_2 supply valve (Valve #2) and then the reactor valve (Valve #4). A leak detection liquid called Snoop was applied to the reactor fittings and the reactor was observed for approximately 5 seconds. If no leaks were suspected (by the appearance of bubbles in the Snoop), the reactor valve was closed, then the cylinder valve was closed, the purge valve opened (Valve #3), and then the reactor valve was opened (Valve #4). The H_2 would vent from the reactor. The sequence was then reversed in order to fill the reactor with H_2. Once the filling/purge sequence was started, Valve #1 was left open. The reactor valve was always opened and closed first during purging in order to prevent back flows of air from entering the reactor from the purge line. This filling and purging cycle was repeated three to five times. During the final filling of the reactor, the cylinder and reactor valves were left open for approximately 10 seconds in order to ensure the reactor was at the full pressure of 4150 kPa and to allow additional time for leak detection. The reactor and cylinder valves were then closed and the reactor was disconnected from the cylinder.

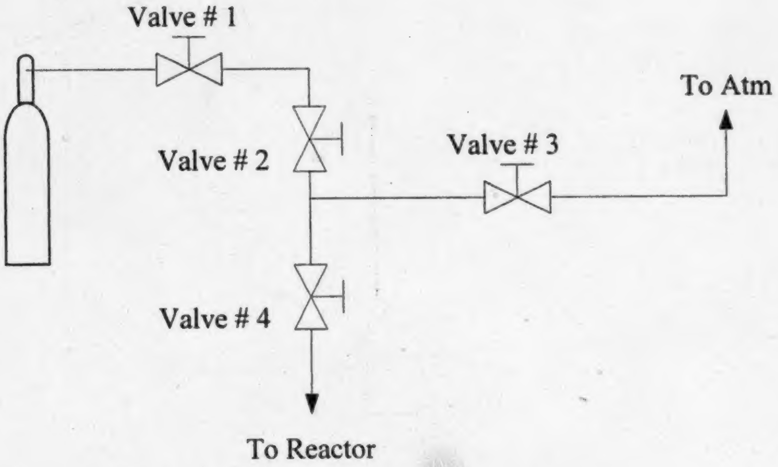


Figure 3.4: Hydrogen Cylinder Valve Schematic

The reactor was then observed for up to another minute and then prepared to be immersed in the sand bath. If at any point in the above sequence a leak from the reactor was noticed, the reactor was disconnected from the H_2 cylinder and the seal was tightened further or loosened and retightened. The H_2 pressurization procedure was then repeated to check the new seal. This procedure rarely was repeated more than three times. If a reactor was becoming problematic during sealing, it was removed from service before there was a risk of it not sealing once feed and catalyst were inside. On the rare event when a reactor could not be sealed or the feed inside the reactor was spilled and the reactor could not be used, it was placed back in the glove bag and the catalyst was removed for use in the next reaction.

3.3.5 Reaction

Once the reactor was loaded and pressurized with 4150 kPa of H_2, it was attached to the rod on the sand bath apparatus and immersed in the sand bath. The connecting arm attached to the rod was then placed on a off-centered cam connected to a motor which caused the reactor to piston up and down at a frequency of about 3 Hz and a total movement of 3 cm. The shaking of the reactor in the sand bath was to promote good mixing inside of the reactor between the H_2, feed, and catalyst. The reactors were left in the sand bath for 30 minutes for the 330 °C reactions, 20 minutes for the 350 °C reactions, and 20 minutes for the 380 °C reactions. At the end of the reaction time, the reactor was removed from the sand bath and then submerged into a water bath to quench the reactions. Once the reactor had cooled, the reactor was removed from the water bath and the product gases were vented into a fume hood. To lower any possible residual H_2S concentration inside of the reactor, the reactor was pressurized with H_2 and then purged to reduce the amount of H_2S in the reactor and ensure a safe concentration of H_2S inside the glove bag.

3.3.6 Product Recovery

After the reaction and purging of the reactor, the reactor was placed into the bench vise and both the top and bottom ends of the reactor were loosened, but not unsealed. The reactor was then placed in the glove bag and the glove bag was sealed and then purged and filled with N_2 as described in Section 3.3.3 above. A funnel was placed into the opening of a vial inside of the glove bag, and if the reaction was not a Cut 8 or Cut 8 nitrogen extract reaction, filter paper was placed in the funnel mouth and the contents of the reactor were emptied into the funnel. The filter paper was used to catch any catalyst pieces that left the reactor with the product oil. For Cut 8 and Cut 8 extract reactions, the product oil was of such a dark color, the catalyst pieces could not be seen in the dark oil in the filter paper and the oil took an excessively long time to filter through the funnel paper. For these reactions, a screen mesh specially fitted inside of a plastic ring was placed inside of the mouth of the funnel before the contents of the reactor were emptied into the funnel. The screen mesh allowed the product oil to quickly flow through the screen and still retained the catalyst pieces for easy recovery. Often the majority of the catalyst pieces stayed near the bottom of the reactor, so the bottom of the reactor was removed and the catalyst pieces were removed with tweezers from the reactor and funnel paper or screen. The catalyst pieces were counted to ensure that all of the catalyst pellets were recovered. The catalyst pellets were placed on a clean paper towel. This served to remove some of the residual oil from the surface of the catalyst. Once all of the pellets were accounted for, they were rolled on the paper towel to remove more of the residual oil. They were then either placed into the next reactor or were put into a vial/jar container in order to be stored in a freezer until the next set of reaction with that catalyst.

The product oil was allowed to flow into the vial from the funnel and the vial was capped for later analysis.

3.3.7 Sample Analysis

The product oil was diluted in methylene chloride and then analysed by GC in order to determine the remaining quinoline concentration in the product oil.

Approximately 0.2 g of the product oil was pipetted into a 10 mL volumetric flask. The volumetric flask was then filled with methylene chloride. 4 mL of this solution was then pipetted using a volumetric pipette into another 10 mL volumetric flask. 3 mL of the internal standard solution was then pipetted in to the second 10 mL volumetric flask.

The second 10 mL volumetric flask was then filled with methylene chloride and mixed. Approximately 1.5 mL of this solution was then poured into a GC autosampler vial. The vial was then placed into the autosampler to be run in the GC.

The internal standard solution was prepared by dissolving 0.0638 g of 2,7-dimethylquinoline in a 200 mL volumetric flask then filled with methylene chloride, resulting in a solution with a $3.19\text{x}10^{-4}$ g/mL concentration of 2,7-dimethylquinoline.

Product oil samples were discovered to age and give decreasing apparent concentrations of quinoline when samples were rerun after being stored in the freezer for over one week. For this reason, product samples were analyzed as soon as possible, usually within 24 hours.

On occasion, during analysis, the integration would return a raw area count for the internal standard that was significantly higher or lower than the other samples before or after the unusual one. This result was usually the result of an unusual baseline. Instead of trying to change the integration method or manually integrating the curves and introducing a source of error into the results, the sample was re-run and the subsequent GC curve integrated, usually resulting in an integration that was consistent with the other samples. Also if an unusually shaped baseline was noted under the quinoline peak but not under the internal standard peak, the sample was re-run even though the internal standard area appeared normal.

Calibration curves for the GC were run frequently during this work. The calibration of the GC showed a slow drift over time as the GC was used, so recalibration was performed in order to ensure all the analysis was as accurate as possible. The drift was attributed to the accumulation and deposit of heavy materials in the GC syringe, inlet, and detector between cleanings. Calibration curves were also run after GC cleaning, preventative maintenance, and repairs. Samples of the feed quinoline and carrier oil mixture were also frequently run in between calibration runs to ensure that the calibration was not changing.

4 Results

4.1 Validation of Experimental Procedure

A number of experiments were performed to ensure that the experimental results obtained were valid and not an artifact of the experimental procedure, set-up, or equipment.

4.1.1 Reactor Temperature and Heat-up Time

In order to determine the temperature of the reactor when it was immersed in the sand bath, special reactors with a thermocouple mounted inside of the reactor were loaded with 3.4 g of carrier gas oil and no catalyst. Because of the nature of the connection of the thermocouple into the reactor, it was not possible to pressurize the reactor with H_2. Because the reactor contents were inert (without catalyst and H_2), the results obtained are different than when the exothermic hydrotreating reactions were occurring. This method would provide a maximum estimate for the time required to heat the reactor. The temperature versus time plot of the reactor with a sand bath temperature of 330 °C is shown in Figure 4.1. The heat-up time was 2 min and 40 seconds. This heat-up time is based on the time it took to heat the reactor to 95% of the steady state temperature (as measured from the starting temperature of 24.7 °C). The oscillatory cycle of temperature that occurred at time greater than 5 minutes was a result of the on/off control of the heater in the sand bath. The controller would heat the sand bath to the set point on the controller and

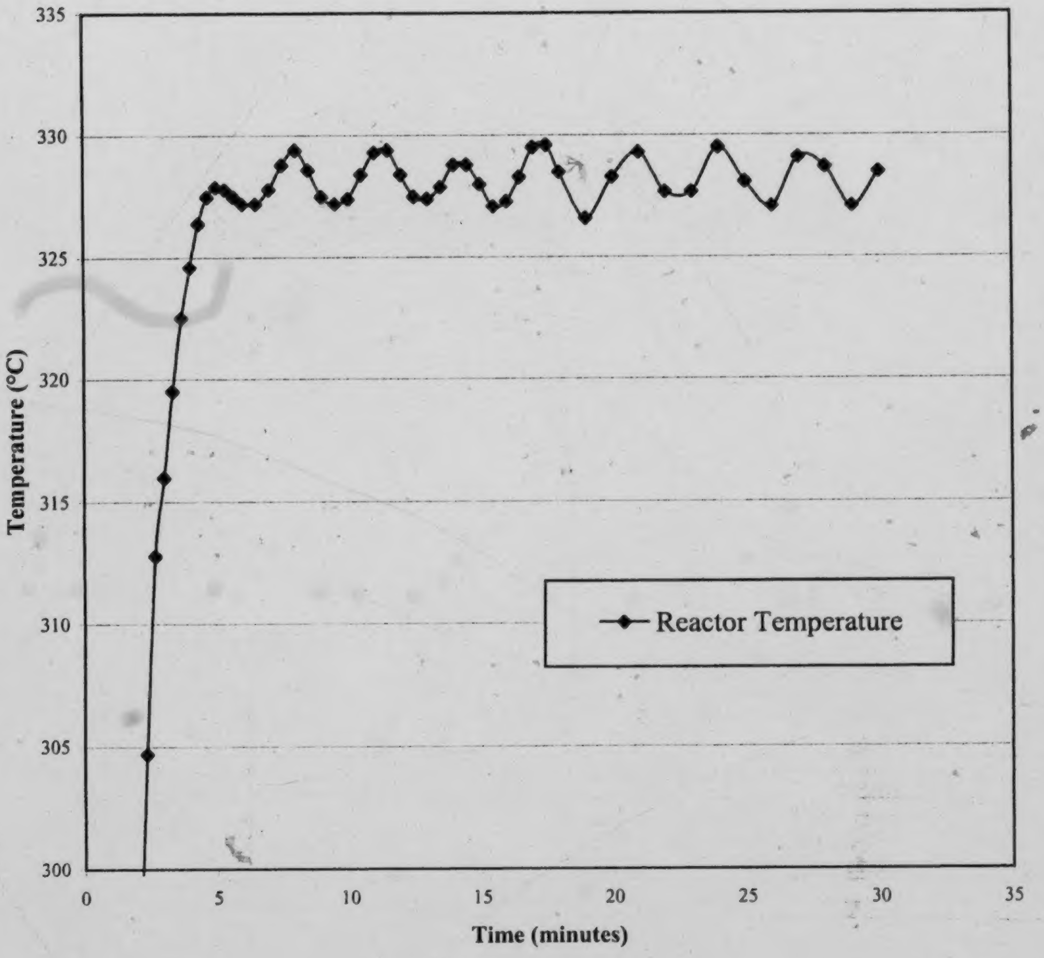


Figure 4.1: Time Course of Reactor Temperature at a Setpoint of 330 °C

then turn the heater off when the set point was reached. The temperature, as recorded by the controller's thermocouple in the sand bath, would continue to increase beyond the set point, as any hot spots near the heating coil were mixed into the rest of the sand bath. The sand would then start to cool until the set point temperature was reached. The heater would turn on but the temperature of the sand would continue to decrease below the set point temperature before it began to heat again. The cycle would then repeat. Figure 4.2 shows the lead-lag between the sand bath controller's thermocouple temperature and the temperature inside the reactor. The cyclic temperature inside of the reactor had a span of 2.5 °C and a period of 3 minutes. This small temperature variation was considered relatively minor compared to the average temperature of 328 °C. The short cyclic periods of 3 minutes also meant that the reproducibility of the experiments should not be significantly affected as each reactor would see a similar number of temperature cycles during reaction, approximately 8 to 10 cycles during the 30 minute reactions. Also important to note is that the average temperature inside of the reactor was 328 °C while the set point of the sand bath was 330 °C.

Heat transfer between the sand bath and the reactor was fairly rapid so the heat generated from the exothermic hydrotreating reactions should be dissipated into the sand bath quickly and should not raise the reaction temperature significantly.

A similar experiment was used to determine the temperature profile in the reactor when the sand bath was set at 385 °C. The time to heat the reactor up to 95% of the final steady state temperature of 365 °C was 3 minutes. A plot of the

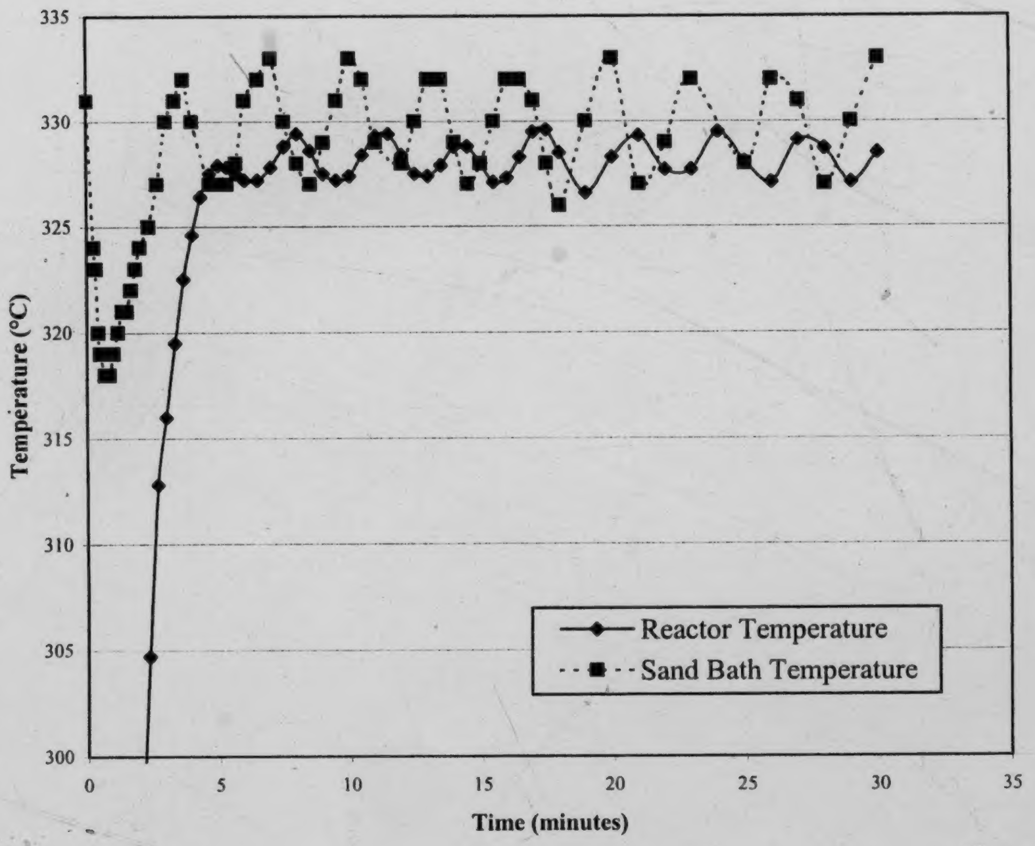


Figure 4.2: Time Course of Sand Bath and Reactor Temperatures at a Setpoint of 330 °C

temperature profile at 385 °C is in Figure 4.3, but the experiment was suspended once the first oscillation cycle was completed. A similar oscillatory temperature cycle was noted, with a period of 3 minutes and a span of 1.2 °C.

The reaction temperatures mentioned in this work (330 °C, 350 °C, and 380 °C) are the temperatures to which the sand bath controller was set. The actual steady state average temperature inside the reactor would be 2-3 °C lower provided the exothermic reactions did not serve to increase the temperature faster than the heat was removed from the reactor to the sand bath.

4.1.2 Repeatability of Results

The results were analyzed in order to check the repeatability of the analysis technique, the gas chromatograph (GC) and the batch reactions themselves. This check offers an error estimate for the GC analysis and the individual batch reactions with a given feed.

4.1.2.1 Repeatability of Results from GC Analysis

For the results obtained from the GC to be considered valid, it was important to discover if the GC, temperature/time program, and the integration method technique used could produce results that were consistent and repeatable. Repeat analysis of reactor samples by GC were used to verify the results and measure the size of the error introduced by the GC and the analysis techniques. Table 4.1 shows the results of such repeat runs, with the calculated percent quinoline converted

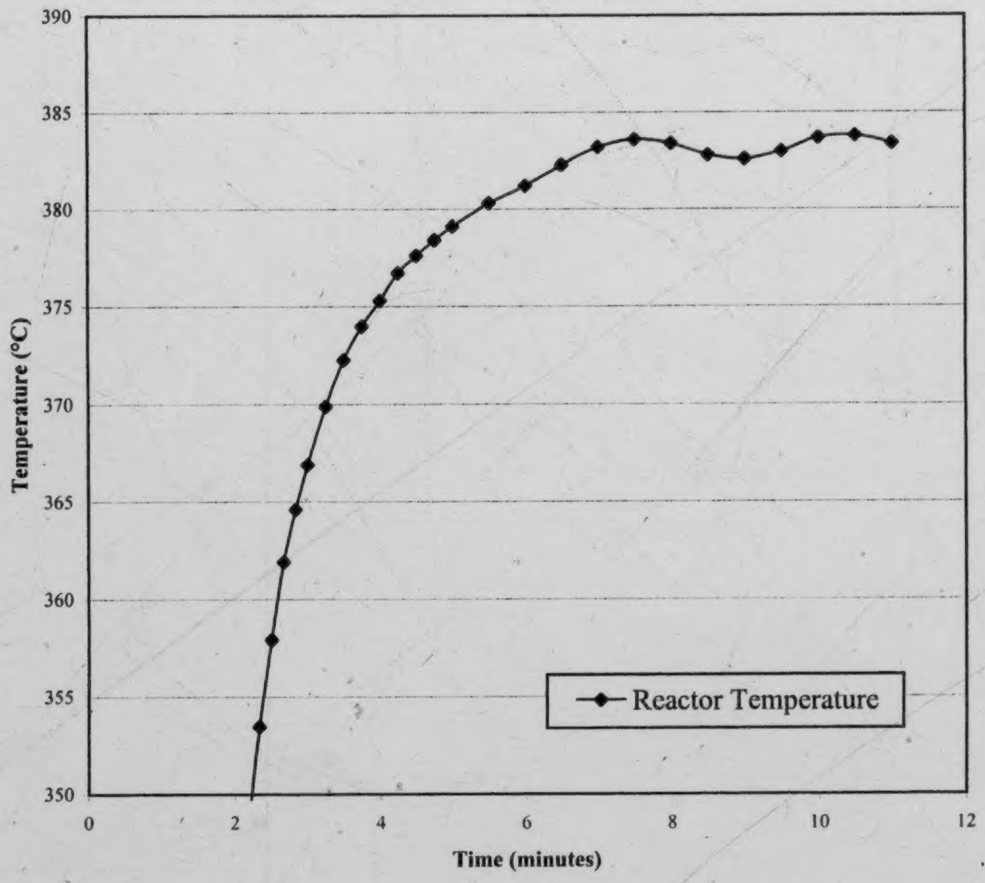


Figure 4.3: Time Course of Reactor Temperature at a Setpoint of 385 °C

shown for the repeat analysis. The average error in these replicates was 1.6 % quinoline conversion, with the maximum error being 3.3 % quinoline conversion. Although most of the experiments were at low conversion, the first replicate was at a high conversion and still showed similar levels of repeatability.

Table 4.1: Sampling of Replicate GC Analysis

Replicate Sample	1st Analysis (% converted)	2nd Analysis (% converted)	Difference (% conversion)	Difference (% concentration)
1-330°C clean feed reaction	54.2	53.0	1.2	2.59
2-330°C Cut 8 reaction	24.4	26.8	2.4	3.27
3-330°C Cut 8 reaction	28.4	27.5	0.9	1.23
4-330°C Cut 8 reaction	17.4	20.7	3.3	4.16
5-330°C Cut 8 reaction	18.4	21.6	3.2	4.07
6-330°C Cut 8 reaction	23.6	24.8	1.2	1.58
7-380°C Cut 8 reaction	20.6	20.4	0.2	0.25
8-380°C Cut 8 reaction	17.3	17.6	0.3	0.36

Since the GC analysis of the amount of quinoline in the samples was shown to be quite reliable, and the GC analyzer time was a valuable commodity, samples were only analyzed twice for the following reasons:

- if there were significant deviations between expected and actual results,
- if an unusual peak or valley occurred near the quinoline or internal standard compound, or
- if the computer program integration of the GC curve was not consistent with the other samples in a series of experiments.

4.1.2.2 Repeatability of Results of Reactor Conversion

Because the reactions were performed with batch reactors, for each feed type a series of reactions were performed. The resulting set of discrete reaction points for each batch reaction exhibited some variance in the quinoline conversion even though they were replicates of each other. For example Replicate Samples 2 through 6 in Table 4.1 were all performed in sequence with the same reactor conditions and Cut 8 feed. However, the quinoline conversions range from 17.4 % to 28.4 % (1st analysis figures). Since there was no reason to doubt any of these results (i.e. a faulty reactor seal), all of the reactions are included in the analysis. For all of the results shown later, all reaction points were used except for points that were suspect due to experimental difficulties and those shown to be outliers statistically (according to the outlier definition of Scheaffer and McClave (1995), detailed in Appendix E). All remaining points were included in the averages for a given feed composition and used to determine the 95% confidence level using the student t-distribution (See Appendix E for details on the 95% confidence level).

When feed compositions were changed, for example from clean feed to Cut 4, the transition from the clean feed quinoline conversion levels to Cut 4 conversion levels was usually very rapid. On occasion, one or sometimes two 'transition' reactions would occur before the new steady state with Cut 4 reactions was noticed. These transition reactions only occurred for the 330 °C reactions. Typically these reactions were excluded from the analysis. Usually, the first reaction with a new feed resulted in a quinoline conversion level similar to later replicate reactions. At the higher reaction temperatures (350 °C and 380 °C) there were no obvious transition reactions. A typical series of reactions performed at 380 °C are shown in Figure 4.4. This reaction series is from the 2000 ppm total nitrogen reactions at 380 °C. Notice the sharp transitions, particularly on the transitions to and from Cuts 8 and 2. The variation in repeated experiments for the same feed can also be noted. The conversions tended to vary around an average, with some points significantly different from the trend or average.

4.1.3 Stability of Quinoline in Reaction System

A reaction was conducted in order to be certain that measurements of quinoline conversion observed after reaction were the result of catalyst activity and not a result of experimental handling, quinoline instability, or reaction due to reactor walls. During this reaction, a new reactor was handled and prepared in a nearly identical fashion as a standard experiment performed in this work with the sole exception that the catalyst was not added to the reactor with the carrier oil, quinoline, and CS_2. The reactor was then placed into the sand bath for 20 minutes at 380 °C. Using the feed (unreacted oil and quinoline mixture) results as a basis, it was observed that after reaction without catalyst, there was a 5.1 % loss of quinoline from the oil and quinoline mixture compared to the feed mixture.

The average GC analysis error between replicate runs is shown to be 2.2 % of quinoline concentration and the largest error between replicate runs was 4.2 % of the quinoline concentration, as shown in Section 4.1.2.1 above. The apparent 5.1 %

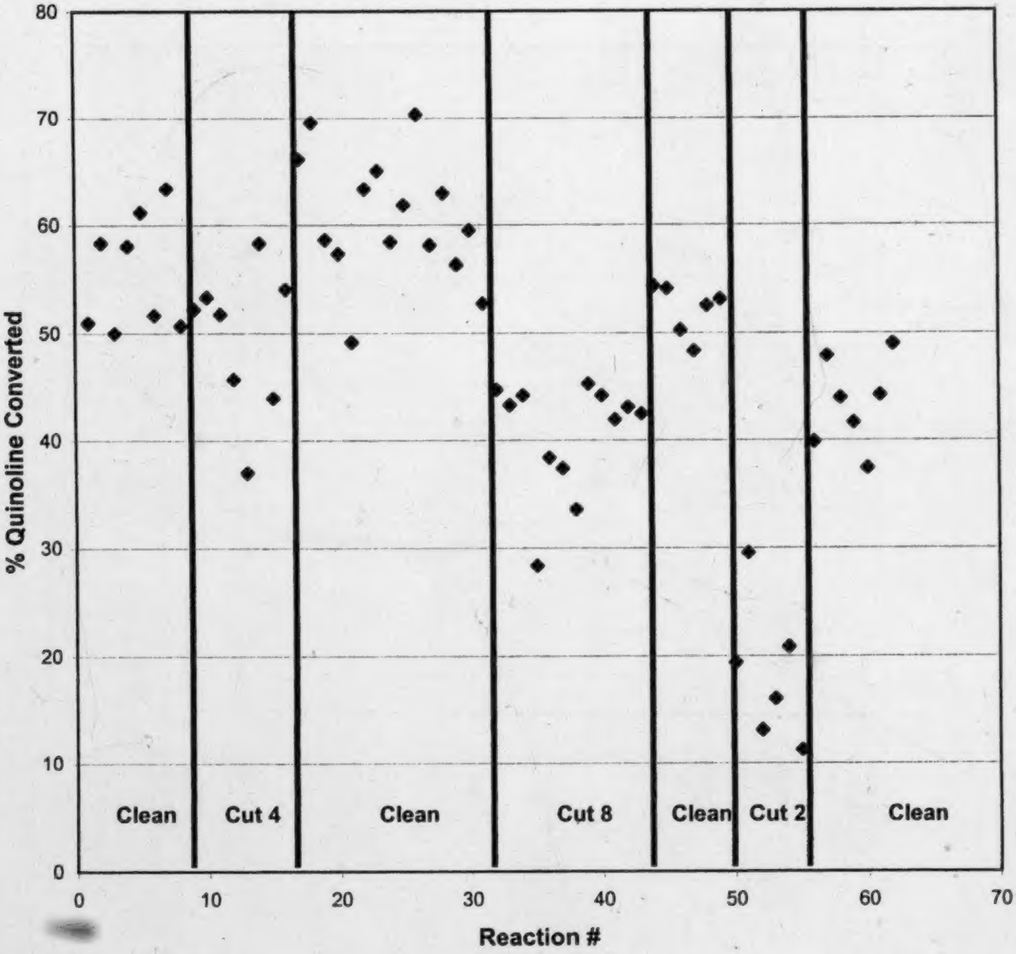


Figure 4.4: Typical Transition Behavior due to Changes in Reactant Concentration (380 °C, 2000ppmN)

loss of quinoline with no catalyst was slightly outside of the range of GC repeatability, indicating some small amounts of quinoline were lost during reaction and handling, but the loss was relatively small compared to the amount of quinoline reacted when catalyst was present. The reduction in quinoline concentration indicates that a minimal amount of quinoline is lost due to decomposition at reactor temperatures. This evidence also shows that only small amounts of quinoline may have volatilized to the atmosphere upon handling during reactor loading and unloading procedures. The new reactor walls were also shown to not act as a catalyst surface and react a significant amount of quinoline. Because these were new reactor walls, there was little metal sulfide on the walls. The comparison between new and old reactors showed there was no difference between new reactors and previously used reactors. (Section 4.1.4 below). Therefore it was considered that any quinoline that disappeared during a reaction with catalyst in the reactor was a result of the catalyst activity only.

4.1.4 Old and New Reactors

Reactors were used for about 10-30 experiments each. As they were used, they accumulated some metal sulfides on the reactor walls. The reactor walls may have gradually gone from the inactive state that was tested above in Section 4.1.3 to an active (catalyzing) state after the metal sulfides had formed. The repeated sealing and unsealing of the reactor fittings made the reactors either very difficult or impossible to seal or nearly impossible to pull apart in order to recover the catalyst.

Therefore the reactors were continually consumed in the progress of this work, and the experiments were performed with reactors of various ages.

To verify that the old reactors were not acting to catalyze the reactions more than the new reactors, whenever an old reactor was replaced with a new reactor in the experimental sequence, the results were examined to ensure that the new reactor did not show a change in apparent activity of the catalyst, either by significantly increasing or decreasing the amount of quinoline converted. Typical results are shown in Table 4.2. Since the new reactor showed no catalyzing effects (Section 4.1.3 above), and there was no difference between the new and old reactors in Table 4.2, it was determined that the metal sulfides on the walls of the old reactors also were not acting to catalyze the reactions. Since there was no difference between the old and new reactors, the statements made earlier regarding the new reactors also applies to the old or sulfided reactors.

Table 4.2: Comparison of New and Old Rectors at the Same Feed Conditions

Feed/Reactor Condition	Old Reactor Average (# of Reactions)	New Reactor Average (# of Reactions)
Cut 4 / 350 °C	35.2 (3)	32.2 (2)
Cut 4 / 380 °C	35.6 (3)	32.2 (1)
2000 ppm N Quinoline	44.5 (1)	43.4 (2)
Clean Feed (after Cut 4 extract) / 380 °C	38.5 (2)	42.0 (2)
Clean Feed / 380 °C	60.5 (1)	61.2 (2)

This changing of the reactors sometimes corresponded with a change in the feed composition, so activities before and after the change in reactors were not directly comparable. Repeated tests had shown that the new reactors had no appreciable difference in activity from the old reactors which were being replaced, therefore, the reactors and feed were changed at the same time with confidence that the results were not being affected by the use of a new reactor.

On the rare occasion when a new reactor showed a difference from the old reactor, it was a very significant and large change in apparent activity of the catalyst. These odd faulty reactors always significantly reduced the apparent activity of the catalyst, since less quinoline would be converted. Two possible explanations for this behavior were considered plausible. The first explanation could be that the new reactor could be leaking H_2 while in the sand bath, lowering H_2 partial pressure and lowering the reaction rate of quinoline. A second possibility is that a portion of the feed oil was trapped and unexposed to the catalyst. For example, if the feed oil was trapped in between the reactor fitting and tube, separated from the catalyst, the quinoline in that volume would not be reacted. Whenever a faulty reactor was suspected, it was removed from service and disposed of.

4.1.5 CS_2 Additions

The catalyst used in HDN reactions was active in the sulfided state and therefore effort had to be made to ensure that the catalyst was always maintained in the sulfided form. Satterfield and Gultekin (1981), Gultekin et al. (1989), plus several others have shown that the amount of sulfur present in the reactor system can affect the rate of HDN reactions. Investigation into the amount of CS_2 required to maintain catalyst activity during the clean feed (sulfur free) reactions was conducted. Since the reactions with gas oil cuts already had high levels of sulfur present due to the sulfur in the cut, it was uncertain what the effects on catalyst activity would be from adding additional CS_2, therefore, reactions with Cut 4 with and without CS_2 were examined.

4.1.5.1 Clean Feed Catalyst Activity with Varying CS_2 Additions

To keep the catalyst in the sulfided state during extended runs with sulfur free, clean feed runs, CS_2 was added to the reactors. To examine the effect of CS_2 on the amount of quinoline reacted, a set of reactions were run with varying levels of CS_2. These reactions were performed early in this work with a feed to catalyst ratio of 4:1 and a temperature of 330 °C. The results are shown in Figure 4.5. As the CS_2 levels increased above 47000 ppm S (addition of 140 μL), the extent of quinoline reaction declined significantly. Since increases in H_2S concentrations are known to increase the rate of HDN reactions, but increases in CS_2 concentrations were lowering the extent of quinoline reacted, it was suspected that the reduction in reaction was due to the consumption of H_2 by the HDS of CS_2. For example, at 200 μL of CS_2 added, the H_2 partial pressure would be reduced by 66 %, but at 30 μL of CS_2, the H_2 partial pressure would only be reduced by 10 %. Because CS_2 was so rapidly transformed to H_2S, the reduction of quinoline reacted was not attributed to occupation of the catalyst sites by CS_2.

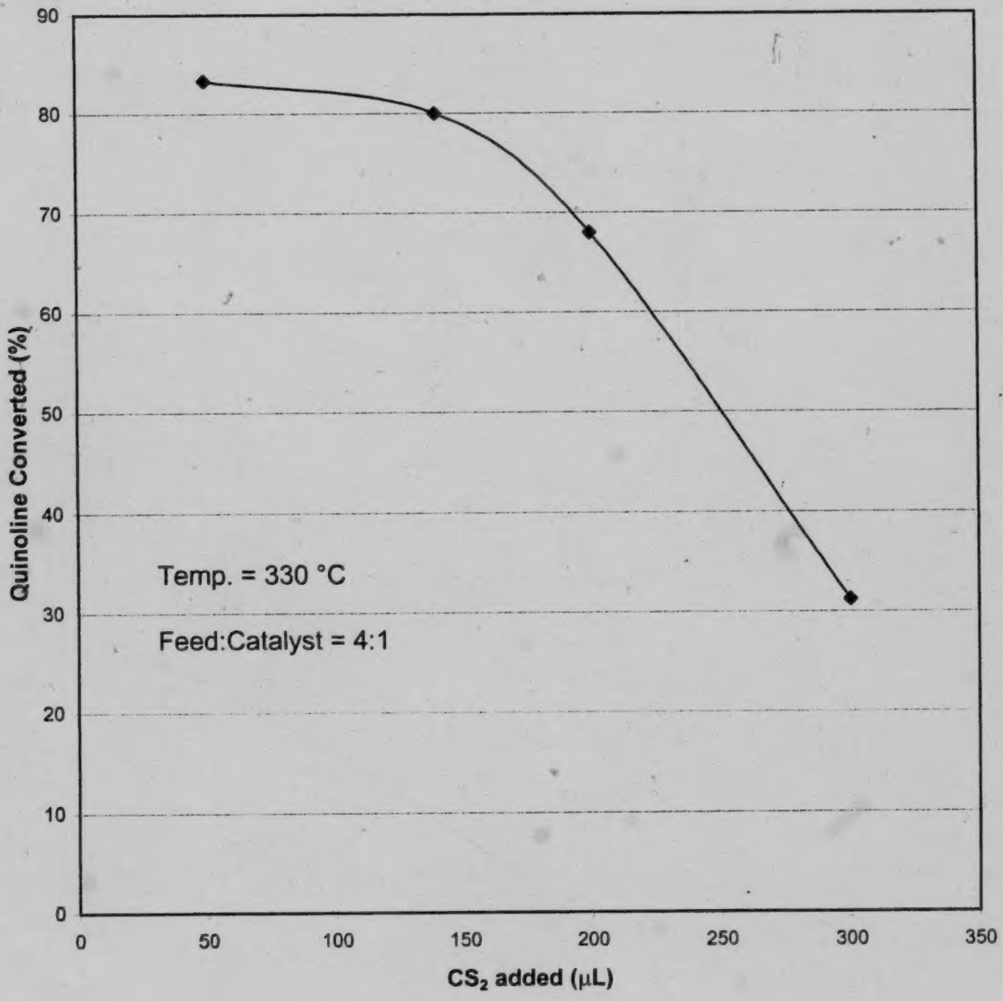


Figure 4.5: Extent of Quinoline Conversion with Varying Levels of Carbon Disulfide

4.1.5.2 CS_2 Addition During Reactions with Gas Oil Cuts

Since the gas oil cuts had high levels of sulfur present during reaction without any CS_2 additions, it was possible that adding CS_2 to the cut reactions would result in a reduction in apparent catalyst activity due to a reduction in the partial pressure of hydrogen, as occurred previously with increasing CS_2 addition levels (Section 4.1.5.1). The effect of adding 30 µL of CS_2 to Cut 4 was investigated at 330 °C and 30 minute reaction times (reaction time includes the heat up time described in Section 4.1.1). Table 4.3 shows the amount of quinoline converted in the presence of Cut 4 both with and without CS_2.

The first two reactions without CS_2 show the transition from clean feed to Cut 4. The next three reactions (without CS_2) had an average of 37.6 % quinoline reacted. The next three reactions had CS_2 present and had an average of 36.5 % quinoline reacted, with no trend in the three reactions up or down.

Table 4.3: Conversion of Quinoline in the presence of Cut 4 with/without CS_2 at 330°C

Reaction #	Without CS_2 (% reacted)	With CS_2 (% reacted)
1	52.2	
2	56.3	
3	34.1	
4	41.8	
5	36.8	
6		38.4
7		34.1
8		37.0

If all of the sulfur in the Cut 4 feed (including both CS_2 and Cut 4 sulfur) was to undergo complete HDS reactions, the partial pressure of H_2 would be reduced by approximately 28 %. The HDS of CS_2 accounts for 10 % of the reduction. This reduction would be equivalent to an 86 μL addition of CS_2. Figure 4.5 showed little reduction in quinoline reactivity until the addition of over 140 μL of CS_2, resulting in a 45 % drop in H_2 partial pressure. The reactions with CS_2 and without CS_2 showed no significant difference (Table 4.3). It was therefore decided to add 30 μL of CS_2 in all subsequent reactions to maintain consistency, and to ensure that enough easily available sulfur was present to keep the catalyst in the sulfided state.

During the reactions with Cut 8 at 330 °C, the addition of CS_2 was forgotten once. Figure 4.6 shows the data from the Cut 8 reactions, the reaction that had no CS_2 added, and the subsequent reactions with Cut 8 that showed a permanent effect on the catalyst activity. A set of reactions is missing due to problems encountered with the GC as it was out of service for a period of time. Forgetting the CS_2 once during the Cut 8 reactions resulted in an immediate reduction in catalyst activity and the reduction was still significant 12 experiments later. This observation provided further justification for adding CS_2 to all subsequent reactions.

4.2 Quinoline Conversion at 330 °C

A summary of reactions performed at 330 °C is shown in Figure 4.7. In this figure, the histogram bars indicate the average amount of quinoline converted

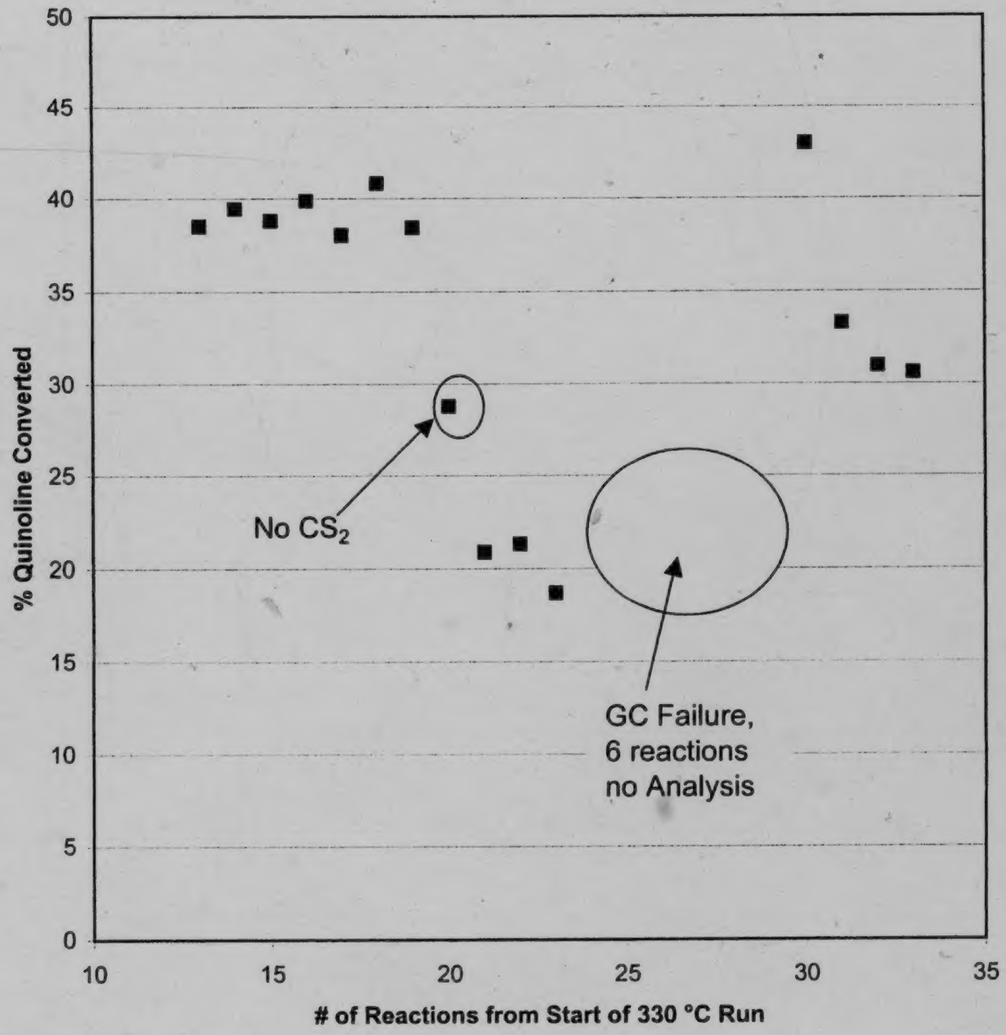


Figure 4.6: Conversion of Quinoline in the Presence of Cut 8 at 330 °C Showing Effect of CS_2 Absence

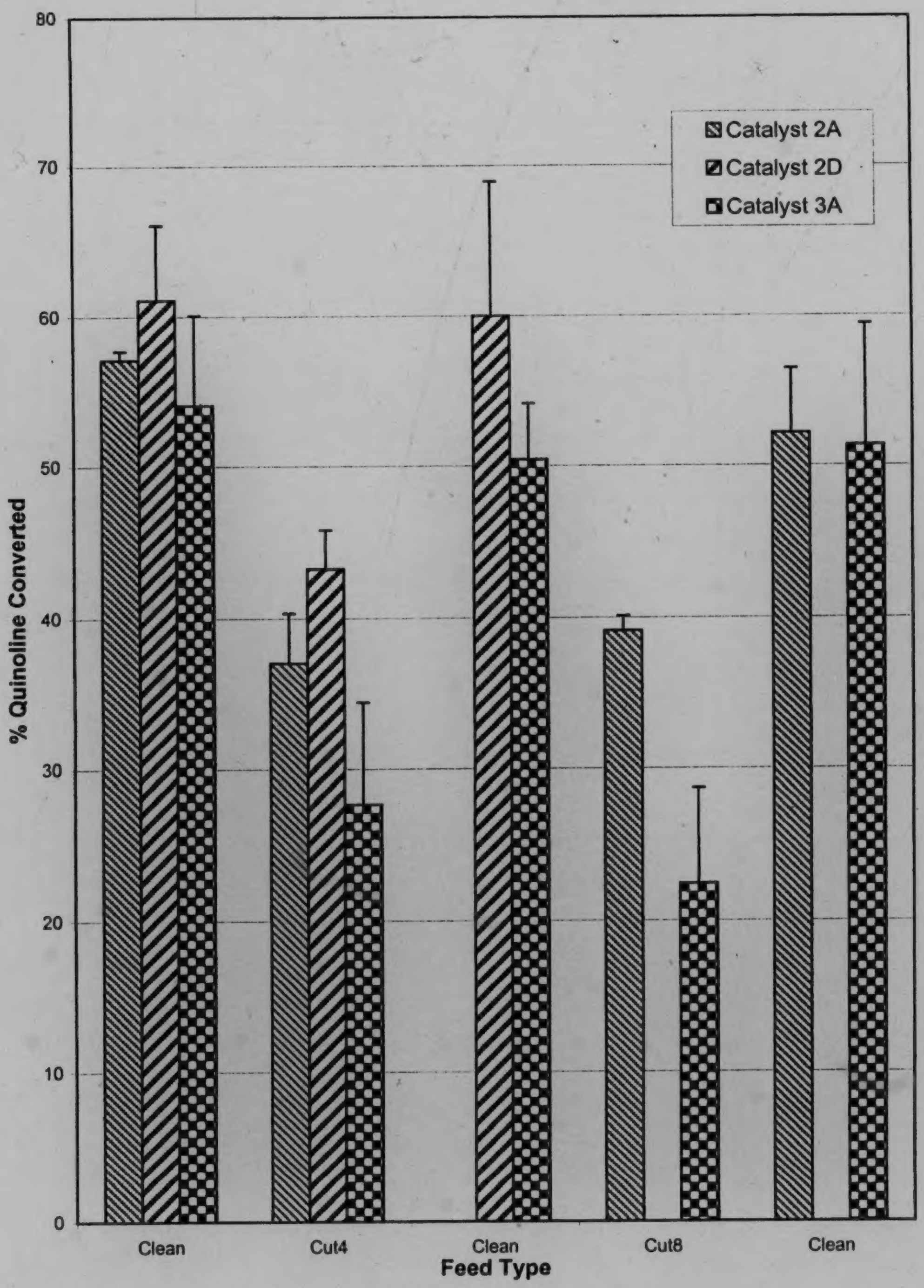


Figure 4.7: Conversion of Quinoline with Different Feed Compositions at 330 °C

during the reactions at that feed condition. The error bars show the "Student's" t-distribution 95 % confidence limits for that average based on the variation during individual reactions in the series at that feed condition. The sequence of the feeds was chosen to enable a comparison of the levels of inhibition between different cuts compared to the clean feed reactions. Reactions with the clean feed after the reactions with each cut, allowed any deactivation due to the cuts to be observed.

Three different catalyst batches were used at this temperature and the results are grouped according to the type of feed to the reactor and the order which the feeds were introduced to the reactor system, with the exception of the third catalyst 3A, where the order of the feeds had the experiments with Cut 8 feed before the Cut 4 feed. Catalyst batches 2A and 2D were subsampled from the same lot of presulfided catalyst, and catalyst batch 3A was from a different lot of presulfided catalyst (See Section 3.3.2). Table 4.4 below illustrates the actual order that the feeds were introduced to the reactor system.

Table 4.4: Order of Reaction experiments for Catalyst Batches at 330 °C

Catalyst	**Feed Order**				
2A	Clean Feed	Cut 4	Cut 8	Clean Feed	
2D	Clean Feed	Cut 4	Clean Feed		
3A	Clean Feed	Cut 8	Clean Feed	Cut 4	Clean Feed

Catalyst batch 2A, the first catalyst sample tested, exhibited good repeatability as shown by the small 95 % confidence bars. This catalyst showed the most consistent reaction to reaction repeatability out of the entire project. This batch of catalyst had been subsampled from a larger batch of catalyst that had been used in some previous microreactor experiments. However, catalyst batch 2D which was also subsampled from the same larger batch of catalyst, exhibited a more typical range of error exhibited throughout the rest of this work. The low error in Catalyst batch 2A was simply attributed to the subsampled batch being of very stable activity for some unknown reason. Because of the low error, these experiments had fewer repeat reactions at each condition than were performed later in this work. The experiments with clean feed as well as the experiments with Cut 4 (with and without CS_2) all used 5 or less experiments at each feed. When an extended series was performed on Cut 8, all seven experiments fell within a range between 38.0 % and 40.8 % quinoline conversion. The eighth experiment with Cut 8 did not have CS_2 added (as mentioned in Section 4.1.5.2 above). Even after the apparent damage to the catalyst from the lack of CS_2, this batch of catalyst still maintained its low variability behavior.

During the experiments with Cut 4 using Catalyst 2A, the effects of CS_2 were studied, as reported in Section 4.1.5.2. Figure 4.7 shows the results with Cut 8 from the experiments prior to the omission of CS_2 (Figure 4.6) and does not include the unusual reactions after the catalyst was deactivated. The data for clean feed results shown in Figure 4.7, after the experiments with Cut 8, include only the last few clean data for feed, when the catalyst activity had recovered to a steady state.

After the Cut 4 and Cut 8 feeds, the return to standard conditions with clean feed, only carrier gas oil and quinoline with no cuts, showed statistically significant reduction in the extent of quinoline conversion. However, since this result was not repeated elsewhere in this work, deactivation was likely a result of the lack of CS_2 in the one Cut 8 reaction.

Catalyst batch 2D was from the same previously reacted batch of catalyst as Catalyst 2A, however, a larger variation between replicates was observed. A similar reduction in the amount of quinoline converted was noted with the addition of the Cut 4 feed as was observed with the previous catalyst batch. After returning to the clean feed (no cuts), the extent of quinoline converted returned to its original level. This result indicated that no permanent deactivation of the catalyst occurred as the result of being in contact with Cut 4. Unfortunately this catalyst was damaged during the removal of the catalyst from the reactor after a reaction. Three or four of the catalyst pellets were crushed and the catalyst batch could no longer be used for further experiments.

Catalyst batch 3A was the first subsample from a freshly sulfided batch of catalyst. This catalyst had not been used in previous batch experiments, unlike the previous two batches (Catalyst 2A and 2D), which had been exposed to some 4:1 feed to catalyst (mass ratio) reactions prior to use in the 25:1 study.

The order of reactions were reversed with this subsample, in order to examine Cut 8 before Cut 4. From the 54.1 % quinoline converted with clean feed, the amount of quinoline converted dropped to 22.4 % with Cut 8 added, a 31.7 % drop in extent of reaction from clean feed conditions.

When Cut 8 was removed and the clean feed was reintroduced, the extent of quinoline converted returned to 50.4 %. This result showed that the exposure to Cut 8 feed resulted in no permanent damage to the catalyst, suggesting that the deactivation noted during the Catalyst 2A reactions with Cut 8 was likely a result of the missing CS_2.

Cut 4 feed was then introduced and the amount of quinoline converted dropped to 27.7 %, a drop of 22.7 %. After removing Cut 4 and reintroducing clean feed, the extent of quinoline converted returned to 51.3 %, once again indicating that no deactivation of the catalyst occurred.

4.2.1 Summary of 330 °C Results

From the reactions performed at 330 °C with Cut 4 and Cut 8, a few key points can be noticed. First, no catalyst deactivation was observed by reaction with either Cut 4 or Cut 8. Second, both Cut 4 and Cut 8 displayed inhibitory effects on the conversion of quinoline. Third, the differences in the amount of quinoline converted in the experiments with Cut 4 and Cut 8 were not statistically significant.

4.3 Quinoline Conversion at 350 °C

The summary results of the experiments performed at 350 °C and a reaction time of 20 minutes (including the heat up time) are shown in Figure 4.8. The histogram bars represent the average of each feed condition and the error bars are the 95 % confidence levels. Since only one catalyst batch was used, the order in

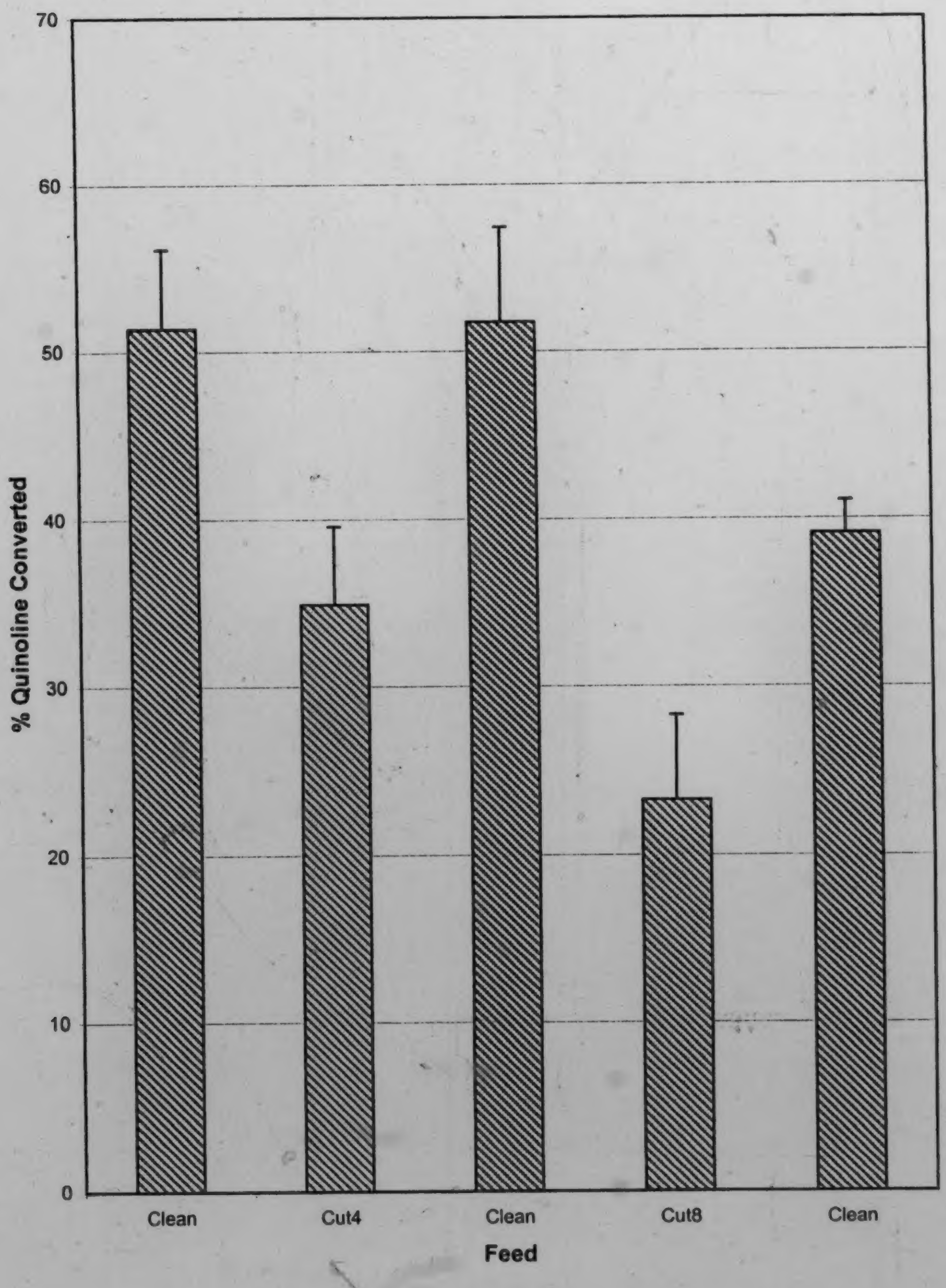


Figure 4.8: Conversion of Quinoline with Different Feed Compositions at 350 °C

which the feeds were introduced to the catalyst is also the order that they appear in the figure. The extent of conversion in experiments with clean feed went from 51.3 % to 34.9 % quinoline conversion when Cut 4 feed was added, and back to 51.8% after Cut 4 feed was removed and clean feed was reintroduced. This result suggests that once again Cut 4 had no permanent deactivation effect on the catalyst.

When the Cut 8 feed was introduced to the catalyst, the amount of quinoline converted dropped to 23.3 %. This level was statistically lower than the Cut 4 feed inhibition (reduction to 34.9 % quinoline reacted). Cut 8 was clearly more inhibitory than Cut 4 at this temperature at the same total concentration of nitrogen in the feed.

When Cut 8 was removed the extent of quinoline converted increased to 39.1 %, giving evidence that Cut 8 had deactivated the catalyst. An extensive series of 14 reactions were performed and this deactivation persisted, suggesting that the reduction in catalyst activity was permanent. This deactivated catalyst was also very consistent in its performance and the extent of reaction fell within a very small range, showing less error than was exhibited during previous replicate runs with this catalyst.

4.3.1 Summary of 350 °C Results

From the experiments performed at 350 °C with Cut 4 and Cut 8, a few key points can be noticed. No catalyst deactivation was observed by reaction with Cut 4, however, some deactivation was apparent after the reaction with Cut 8. Both

Cut 4 and Cut 8 displayed inhibitory effects on the conversion of quinoline. Cut 8 exhibited a statistically higher amount of inhibition than Cut 4.

4.4 Quinoline Conversion at 380 °C

Much more work was performed at the reaction temperature of 380 °C, because commercial hydrotreating reactions run at elevated temperatures closer to 380 °C. An additional cut was examined (Cut 2), as well as nitrogen extracts from Cut 4 and Cut 8. A reaction series with half of the cut concentration (total nitrogen concentration of 2000 ppm) was also performed as well as a reaction series with varying quinoline concentrations. The experiments with varying amounts of initial quinoline concentration were performed in order to verify the reaction kinetics of the quinoline reactions.

4.4.1 Quinoline Conversion with 3000 ppm total Nitrogen

The summary of results of the experiments performed at 380 °C and 20 minutes with a total nitrogen concentration of 3000 ppm are shown in Figure 4.9. This nitrogen concentration is the same as the experiments performed at 330 °C and 350 °C. The format for the figure is the same as that for the 350 °C temperature reactions in Figure 4.8.

The results of experiments with clean feed went from 52.2 % quinoline converted to 35.0 % quinoline converted when Cut 4 was introduced. Once the Cut 4 feed was removed, the amount of quinoline converted increased back to

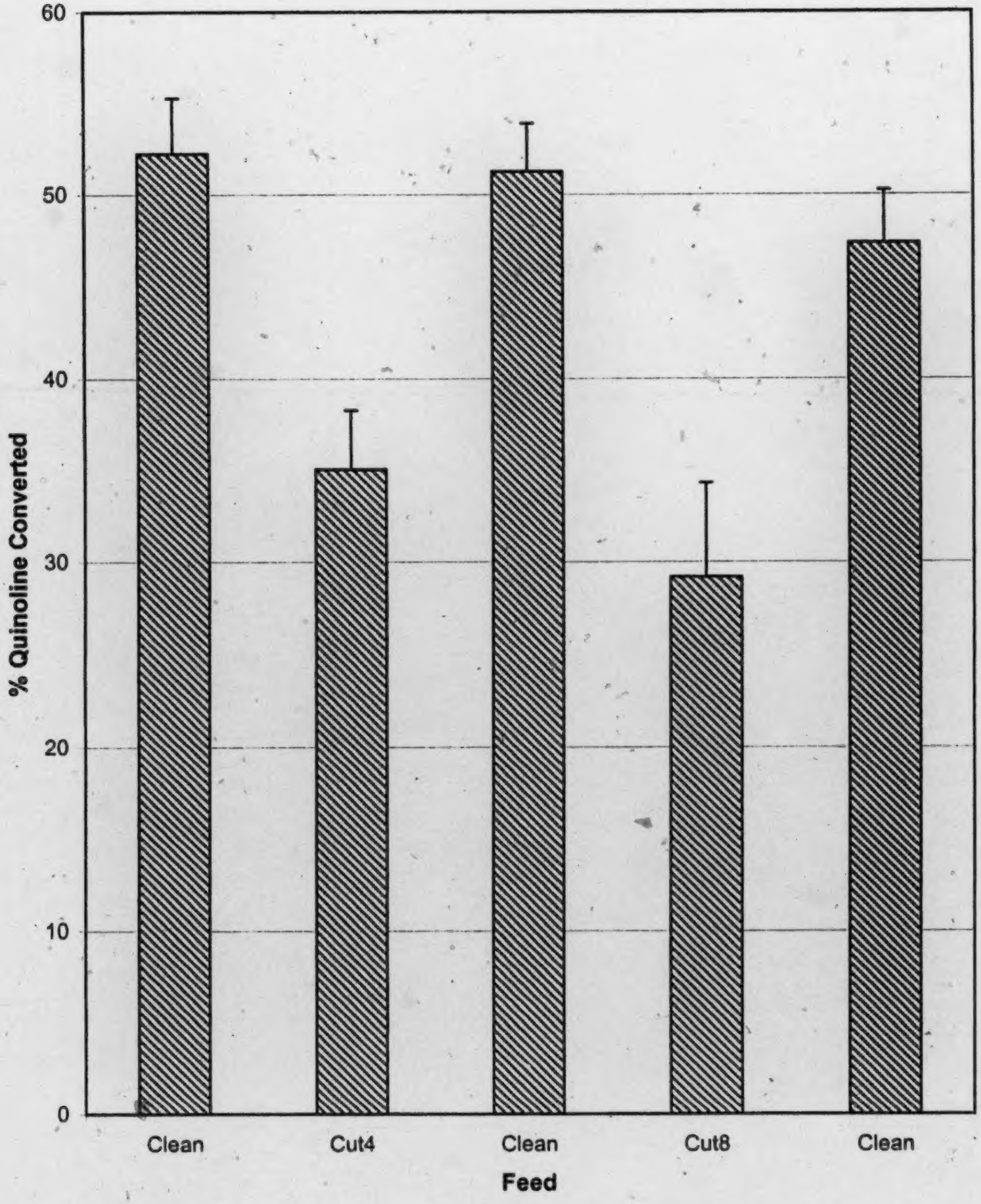


Figure 4.9: Conversion of Quinoline with Different Feed Compositions at 380 °C

51.3 % when clean feed was reintroduced. This result once again showed that Cut 4 exhibits no catalyst deactivation effects.

When Cut 8 feed was introduced to the catalyst, the amount of quinoline converted dropped to 29.2 %. This average was 5.8 % below the average value with Cut 4, however, the 95 % confidence intervals on the student t-distribution overlap indicating that the difference cannot be certain with 95 % confidence. After the Cut 8 was removed and clean feed reintroduced, the amount of quinoline reacted increased to 47.3 %. This was 4 % below the experiments before Cut 8 was added, however, the deactivation of the catalyst due to Cut 8 was not significant.

At this point it was decided to examine the effects of Cut 2 on catalyst conversion. Since the catalyst batch used above was required for testing other feeds, a new catalyst batch was used and the results of the 3000 ppm of total nitrogen study with Cut 2 feed is shown in Figure 4.10. The average extent of quinoline reacted dropped from the typical value of 50.4 % to 17.5 % when Cut 2 was present in the feed. This 32.9 % drop in the amount of quinoline reacted was greater than the 17.2 % drop with Cut 4 and the 22.1 % drop for Cut 8 on the previous catalyst. Before each cut, the two catalyst batches showed similar initial activities (52.2 % and 51.3 % quinoline converted (Cut 4 and Cut 8) compared to the 50.4 % quinoline conversion for this catalyst batch). Cut 2 gave the most significant reduction in the amount of quinoline reacted, and therefore exhibited the most inhibitory effect on the catalyst of the three cuts examined.

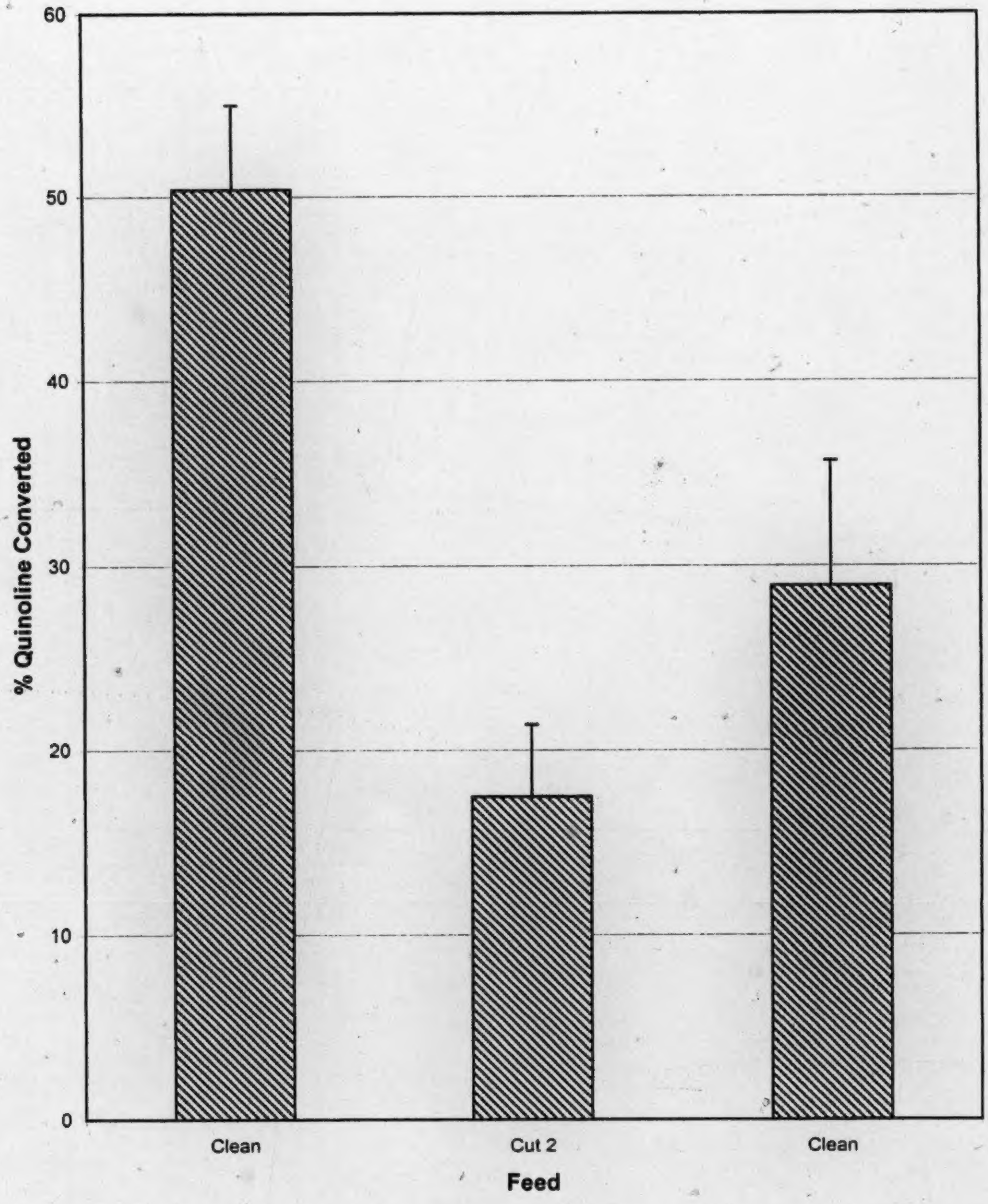


Figure 4.10: Conversion of Quinoline with Cut 2 (3000 ppm Total Nitrogen) at 380 °C

When Cut 2 was removed, the amount of quinoline converted recovered only slightly to 28.9 %. The poor conversion after Cut 2 was removed indicates a very severe deactivation of the catalyst and the deactivation continued even after an extended sequence of 12 experiments with clean feed. Since the catalyst was deactivated, it was not possible to have a starting point for a comparison with Cut 4 on the same catalyst. Due to time and feed availability constraints, it was not possible to repeat the 3000 ppm total nitrogen Cut 2 reactions with a catalyst that had already been reacted with Cut 4 to directly compare the two different cuts on the same catalyst. However, because the two catalyst batches had similar initial activities with clean feed, comparing the two sets of data is appropriate. The complete series of Cuts 2, 4, and 8 were completed on one catalyst at 380 °C and 2000 ppm total nitrogen as shown below in Section 4.4.2.

4.4.2 Quinoline Conversion with 2000 ppm total Nitrogen

Although most of the work in this project used a total nitrogen concentration of around 3000 ppm nitrogen, with 1080 ppm due to quinoline and 1900 ppm due to the cuts, it was decided to examine the effects of concentration of the cut, (or total nitrogen concentration). Reactions similar to the 3000 ppm reactions were performed, but only half of the cut that was used previously for the 3000 ppm total nitrogen concentration was used. This reaction series with lower concentrations of cuts would help show if cuts had reached a maximum inhibition plateau or if the effect was concentration dependent. The summary results of the reactions with different feeds and a total nitrogen concentration of 2000 ppm are shown in Figure 4.11. This figure shows the average extent of quinoline conversion at each feed condition. The order that the feeds appear in the figure was the same as they were introduced to the catalyst.

In the clean feed, 55.5 % of the quinoline was converted at the start of the 2000 ppm study. When Cut 4 was introduced, that average fell to 49.5 %, but the difference was not statistically significant at the 95 % confidence level. Once Cut 4 was removed and clean feed reintroduced, the amount of quinoline reacted increased to 60.6 % which was higher than the starting reactivity of the catalyst. The clean feed quinoline conversion before Cut 4 was added had an average of 55.5 %. The pre-Cut4 clean feed average of 55.5% had 4 reactions with 58 to 63 % conversion and another 4 reactions with a 50 to 51.5 % quinoline conversion. All 8 reactions were included in the average and the 95 % student t-distribution confidence levels, since there was no reason to suspect that any of the points were invalid. No reasonable pattern could be established for the two separate steady states so no set of reactions could be discounted. Because of this apparent dual steady state condition, the increase in the clean feed reactions after Cut 4 and the decrease in the clean feed reactions after Cut 8 cannot be used to draw conclusions on the deactivation/enhancement of the catalyst.

The conversion of quinoline dropped to 40.6 % when Cut 8 was in the feed and then recovered to 52.1 % quinoline conversion when the clean feed was reintroduced.

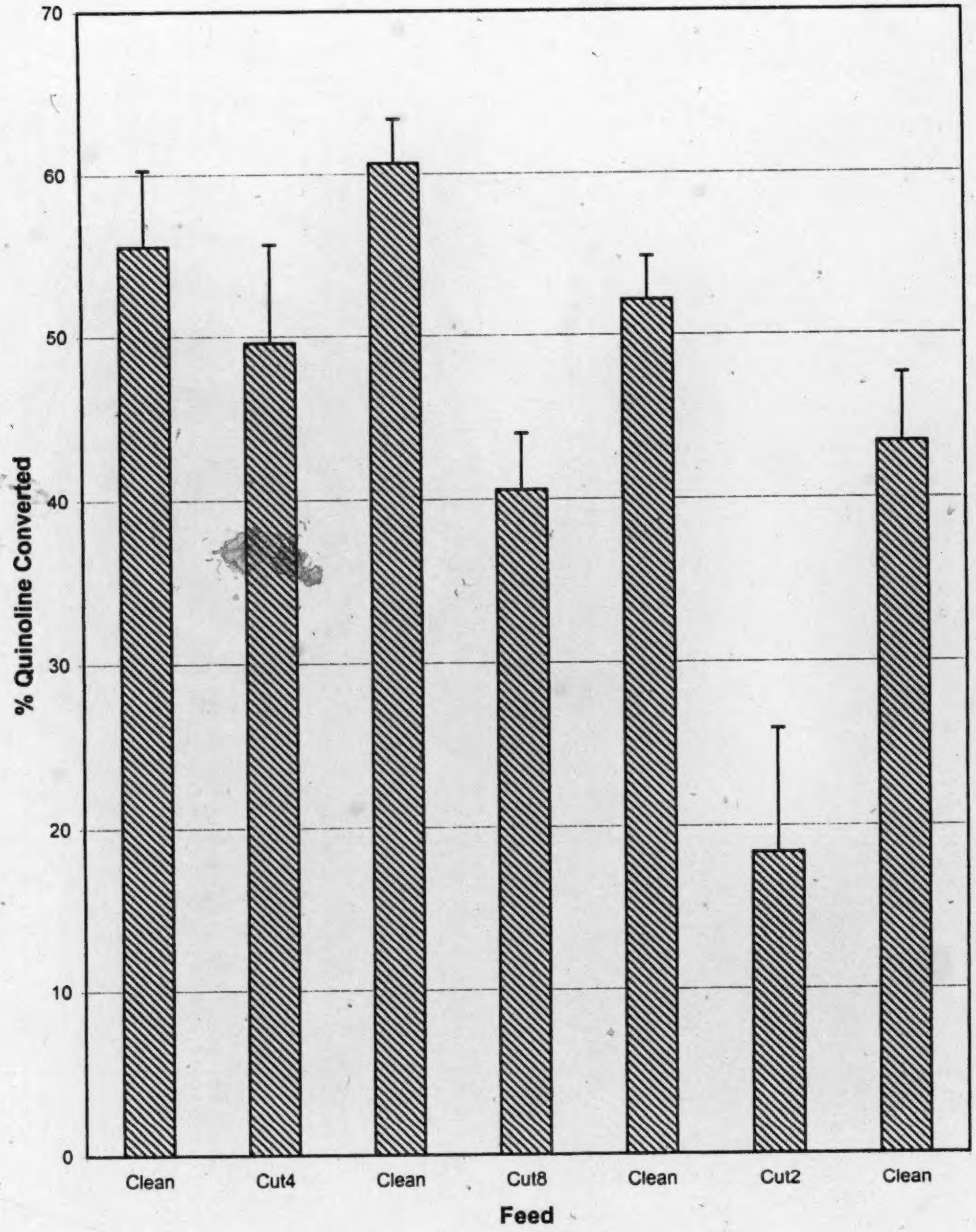


Figure 4.11: Conversion of Quinoline with Different Feeds at 380 °C (2000 ppm Total Nitrogen)

Cut 2 was then added as feed to the system. The amount of inhibition was once again, as in the 3000 ppm total nitrogen study, more significant than either Cut 4 or Cut 8. Although there was greater variability in the data with the Cut 2 feed, the inhibition was a 33.7 % drop in quinoline conversion to only 18.4 % quinoline conversion. Compared with the Cut 8 extent of reaction of 40.6 %, the magnitude of the inhibition was surprising and statistically significant. After clean feed was reintroduced, the amount of quinoline reacted recovered to 43.4 %, still 8.7 % less conversion than before Cut 2 was introduced to the catalyst, indicating statistically significant deactivation. The behavior of Cut 2 in these experiments was similar, therefore, to the data obtained from the 3000 ppm total nitrogen reported in Section 4.4.1 above.

4.5 Reaction Kinetics for Quinoline Conversion

Kinetic information on the quinoline conversion was obtained by varying the initial quinoline concentration during one of the reaction series. The variation in quinoline concentration was also performed in order to verify that no unusual behavior was noted that could be attributed to changing reactor conditions such as a reduction of H_2 partial pressure. As the total nitrogen concentration increased, due either to the presence of cuts or higher quinoline concentrations, an increase in HDN reactions and H_2 consumption could exhibit an effect on the apparent catalyst activity similar to the effects of CS_2 concentration shown in Section 4.1.5.1.

The concentration of quinoline in the reactor was varied from 0.5 wt% to 2.74 wt% from 3.87×10^{-5} to 2.12×10^{-4} moles of quinoline per gram of reactor feed (mol Q/g feed). By using LHHW type catalyst behavior equations, Equation 4.1 can be developed. (See Appendix D for more detailed kinetic equation development). In Equation 4.1, the term k, includes items such as catalyst weight and weight of feed, since the ratio of feed to catalyst was always constant at 25 to 1. The results of varying the quinoline concentration were used to obtain kinetic information to build the reaction rate equations.

$$rate = \frac{akC}{1+KC} \qquad \text{Equation 4.1}$$

Equation 4.1 was integrated and the Equation 4.2 was developed.

$$\frac{C_o - C_t}{t} = \frac{1}{Kt}\ln\frac{C_t}{C_o} - \frac{ak}{K} \qquad \text{Equation 4.2}$$

Where a is the activity of the catalyst, k is the reaction rate constant, K is the adsorption constant, C_t is the final quinoline concentration after reaction, C_o is the initial quinoline concentration before reaction, and t is the length of the reaction time (in minutes). Both k and K include other constants lumped in beyond just the reaction or adsorption constants (see Appendix D for more information). For the varying quinoline concentration reactions, the catalyst was assumed to have an activity of 1. The values of $(C_o-C_t)/t$ were plotted vs. $\ln (C_t/C_o)$ and Microsoft Excel was used to determine the slope and intercept of the line (a least sum of squares regression). The values of k and K were then determined from the slope and intercept. The values of k and K were 5.97×10^{-2} g feed^{1} g cat^{-1} min^{-1} and

1.08×10^4 g feed^1 mol Q^{-1}, respectively. Because the average quinoline conversions for the 0.5 wt% reactions did not fit the kinetic analysis for k or K well, it was excluded from the calculation. The low quinoline concentration (0.5 wt%) reactions, displayed a very large variability and the GC analysis of the residual quinoline concentration after reaction was subject to increased error.

Figure 4.12 shows the actual and predicted average quinoline reaction rates as a function of initial quinoline concentration. The model does not predict average reaction rate well for low initial quinoline concentration (0.5 wt% quinoline). However, a plot of predicted and actual quinoline concentration after reaction in Figure 4.13 shows that the prediction does a reasonable job of predicting the amount of quinoline remaining, even for the 0.5 wt% reactions. Because of the low initial concentration of quinoline in the 0.5 wt% reactions, small errors in measuring the final concentration after reaction leads to large errors in the average quinoline reaction rate values, however the resulting final concentration of quinoline is relatively close.

The close fit between the experimentally determined rate of quinoline reaction and the LHHW model with optimized constants shows that the LHHW kinetics can be used to represent and predict the quinoline reactions performed during this study.

The value of k and K fit well with the values determined by Miller and Hineman (1984) for quinoline HDN. They reacted quinoline at a concentration of 1780 to 9650 ppm nitrogen due to quinoline in a carrier gas oil (with less than 1

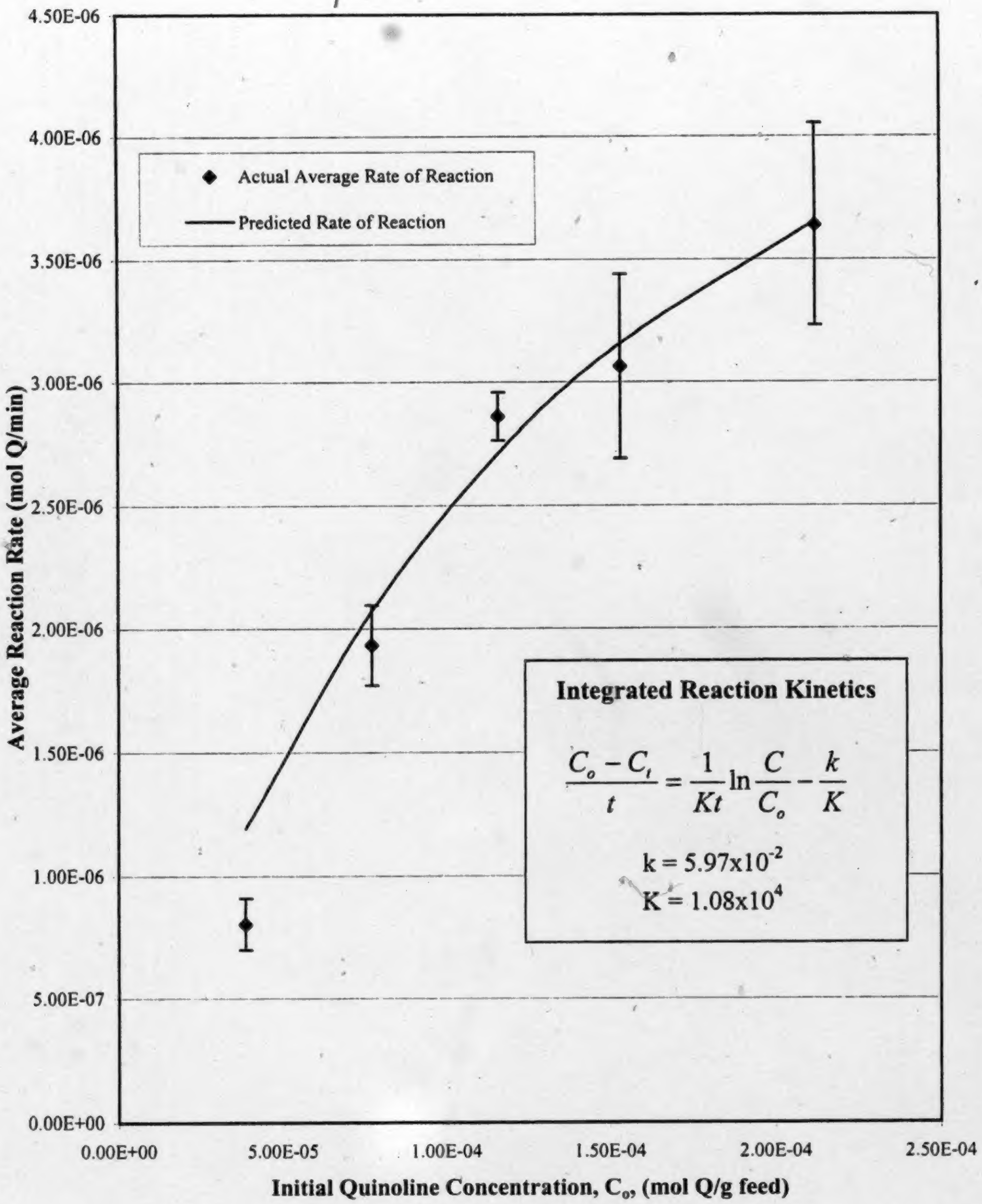


Figure 4.12: Actual and Predicted Average Quinoline Reaction Rate

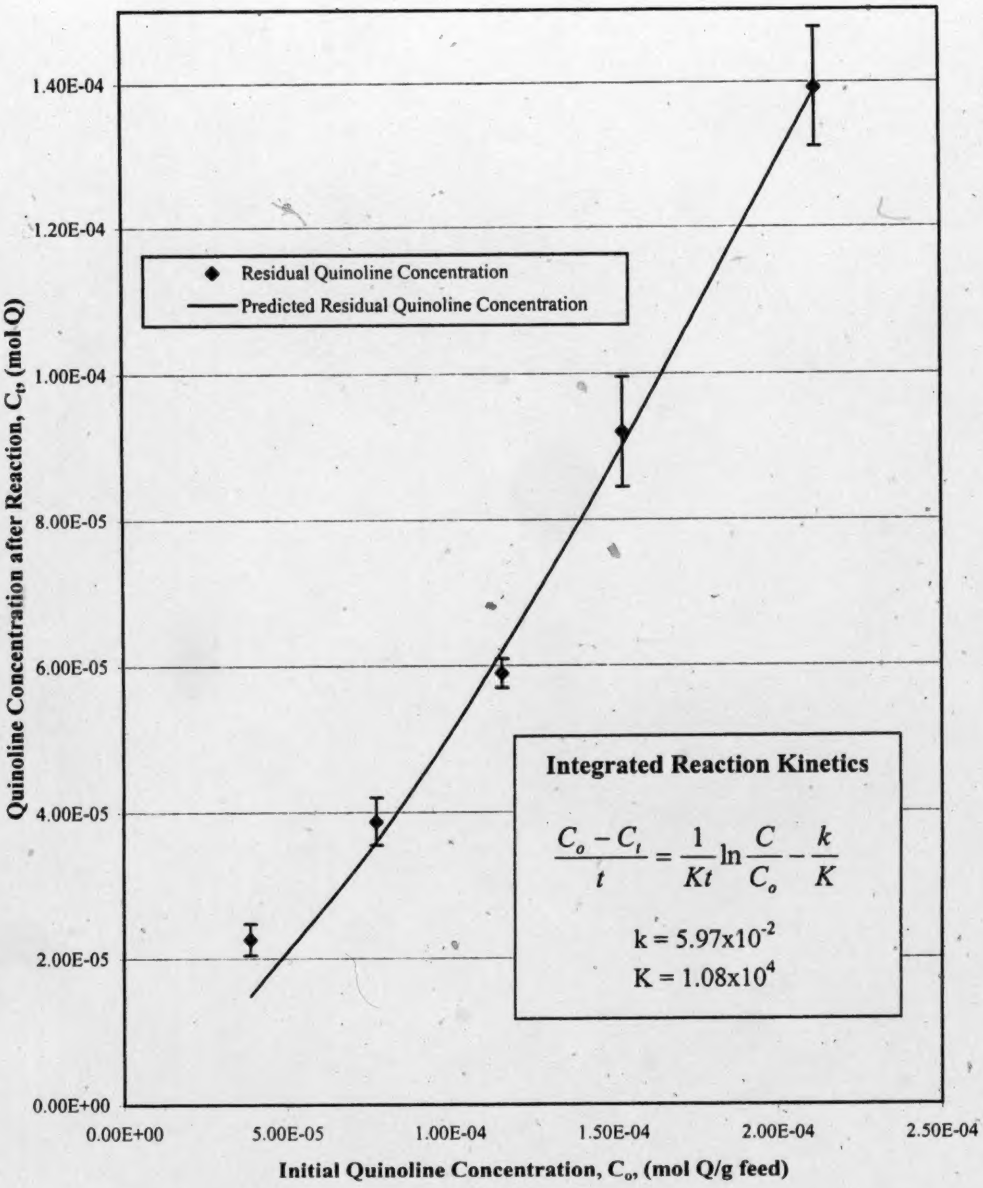


Figure 4.13: Actual and Predicted Residual Quinoline Concentration after Reaction

ppm sulfur and nitrogen). The reactions above range from 1080 to 3200 ppm nitrogen due to quinoline in a low sulfur, low nitrogen gas oil. The reaction over a crushed CoMo catalyst on two different supports at 375 °C resulted in a K value of $1.7\text{x}10^3$ to $2.3\text{x}10^3$ g feed^1 mol Q^{-1}, assuming in their work the units of K were ppm (g Nitrogen / g Feed). The value of K in Miller and Hineman's work was an order of magnitude lower the value determined during this work. Interesting to note is that Girgis and Gates (1991) reports the K value for the Miller and Hineman work as $1.7\text{x}10^4$ and $2.3\text{x}10^4$, an order of magnitude higher and very close to the values determined by this work, but apparently in error. The reaction rate constant by Miller and Hineman (1984) was reported in units of cm^3 feed/cm^3 cat/hr, which could not be easily converted to comparable units, since the required information was not given. Assuming a feed density of carrier oil of 0.9 g/cm^3 and a bulk catalyst density of 0.7 g/cm^3 (as shown in a similar sized crushed catalyst by Satterfield et al. (1980)), a value of k was between $2.2\text{x}10^{-2}$ and $3.9\ \text{x}10^{-2}$ g feed^1 g cat^{-1} min^{-1}, which is only slightly below the reaction rate constant calculated above. The lower reaction rate constant would make sense as the CoMo catalyst should not promote HDN reactions as well as the NiMo catalyst used in this work.

Other work also gave comparisons for the k and K values, although most of the other work was the result of reacting quinoline in a pure solvent carrier (n-hexadecane). Gioia and Lee (1986) report a value for K as $1\text{x}10^5$ g feed^1 mol Q^{-1}, an order of magnitude larger than the value determined during this work. Satterfield and Smith (1986) suggest that quinoline is in equilibrium with 1,2,3,4-tetrahydroquinoline, so the reaction rate is not shown for quinoline directly. If however, quinoline and 1,2,3,4-THQ are considered together in Satterfield and Smiths work, the reaction rate constant, k, for the combined components is 7.3×10^{-1} g feed^{1} g cat^{-1} min^{-1}, which is significantly higher than in this work.

4.5.1 Kinetic Analysis of Inhibition by Narrow Cuts of Gas Oil (3000 ppm total Nitrogen)

In order to obtain some information on the inhibition kinetics of the various cuts, the inhibition effects of the cuts were assumed to follow LHHW kinetics where the overall rate of reaction equation would be in the form of Equation 4.3

$$rate = \frac{kC}{1 + KC + K_I I} \qquad \text{Equation 4.3}$$

The values of k and K were determined in Section 4.5 as 5.97×10^{-2} g feed^{1} g cat^{-1} min^{-1} and 1.08×10^{4} g feed/mol Q respectively (where I = 0). The value of k determined in Section 4.5 is a lumped constant, which includes the terms shown in Equation 4.4. The term k_r is the net reaction rate constant of the quinoline reactions. All experiments used the same mass ratio of feed to catalyst (25 to 1), therefore the ratio of the mass of feed to catalyst is constant. The value of k determined in Section 4.5 includes the mass ratio constant.

$$k = \frac{k_r m_{feed}}{m_{cat}} \qquad \text{Equation 4.4}$$

Because these values of k and K were not determined for each catalyst batch, the activity 'a' is used to account for differences in catalyst activity of different catalyst batches and is shown in Equation 4.5 below. The value of k determined in Section 4.5 above assumed the catalyst had an activity of 1.

$$rate = \frac{akC}{1 + KC + K_I I} \qquad \text{Equation 4.5}$$

The rate equation (Equation 4.5) is the same as the following differential equation shown in Equation 4.6.

$$-\frac{dC}{dt} = \frac{akC}{1 + KC + K_I I} \qquad \text{Equation 4.6}$$

Because the reaction rate (disappearance rate) of the inhibitor 'I' was not measured, an approximation for the concentration of I was needed. It was assumed the concentration did not change, and could be represented by the initial concentration of the inhibitor. Equation 4.6 was integrated and the results are shown in Equation 4.7 below.

$$\frac{C_o - C_t}{t} = \frac{(1 + K_I I)}{Kt} \ln\frac{C_t}{C_o} - \frac{ak}{K} \qquad \text{Equation 4.7}$$

The catalyst activity was determined from the clean feed reaction set immediately following the cut reaction by using the previously determined values of k and K. The following clean feed reactions were chosen instead of the preceding clean feed reactions in order to minimize errors due to small deactivations in Cut 4 and Cut 8 and to determine an inhibition value for Cut 2, which had deactivated the catalyst significantly. The activity of the catalyst before and after the Cut 2 reactions was calculated in order to determine the extent of deactivation. Once the activity of the catalyst was determined, the reaction series with the cut was examined using Equation 4.7 and the value of K_I determined for each cut. Table 4.5. shows the key kinetic information for the 3000 ppm total nitrogen reactions.

Table 4.5: Cut Inhibition Kinetics for 3000 ppm Total Nitrogen

Cut	k	K	a	C_o (mol Q/g feed)	I (g Cut/g feed)	K_I (g feed/g Cut)
Cut 2	5.97×10^{-2}	1.08×10^{4}	0.481	7.74E-05	0.794	1.60
Cut 2**	5.97×10^{-2}	1.08×10^{4}	0.924	7.74E-05	0.794	5.11
Cut 4	5.97×10^{-2}	1.08×10^{4}	0.945	7.74E-05	0.456	2.14
Cut 8	5.97×10^{-2}	1.08×10^{4}	0.854	7.74E-05	0.282	4.60

** Activity determined from clean feed reactions **before** Cut 2 Reaction

From Table 4.5, it can be seen that Cut 8 is much more inhibitory than Cut 4 on a per gram basis. Based on K_I, Cut 8 is 2.1 times more inhibitory per gram cut than Cut 4. The inhibition of Cut 2 (as determined by using the deactivated catalyst activity of 0.481) is approximately as inhibitory as Cut 4. However, important to note is that Cut 2 deactivated the catalyst significantly. The activity of the catalyst before Cut 2 was introduced to the catalyst was 0.924, however, after the Cut 2 reactions, the activity was reduced to 0.481, a 47.9 % decrease in catalyst activity.

Error bounds were determined for each K_I by using the experimentally determined 95% student-t confidence limits determined from each reaction series. From the 95% confidence interval of the inhibition reactions, the upper and lower range of the quinoline reaction rate was determined and then the K_I was determined for both the upper and lower reaction rates. The analysis showed the following K_I ranges displayed in Table 4.6.

Table 4.6: Error Range fore K_I as Determined by 95% Confidence Level

Cut	Average K_I (g feed/g Cut)	Lower K_I (g feed/g Cut)	Upper K_I (g feed/g Cut)
Cut 2	1.60	0.463	4.19
Cut 2**	5.11	3.45	7.98
Cut 4	2.14	1.66	2.70
Cut 8	4.60	3.50	5.94

** Activity determined from clean feed reactions **before** Cut 2 Reaction

4.5.2 Kinetic Analysis of Inhibition by Narrow Cuts of Gas Oil (2000 ppm total Nitrogen)

The kinetics of the cut inhibition for the 2000 ppm total nitrogen was performed. Using the same equations (Equation 4.7) and the same K_I as shown in Table 4.5 determined from the 3000 ppm study. Table 4.7 shows the selected components of Equation 4.7.

Table 4.7: Cut Inhibition Kinetics for 2000 ppm Total Nitrogen

Cut	k	K	a	K_I (g feed/g Cut)	Actual C_t (mol Q/g feed)	Predicted C_t (mol Q/g feed)
Cut 2	$5.97\text{x}10^{-2}$	$1.08\text{x}10^{4}$	0.769	1.60	$6.32\text{x}10^{-5}$	$5.19\text{x}10^{-5}$
Cut 2**	$5.97\text{x}10^{-2}$	$1.08\text{x}10^{4}$	0.966	5.11	$6.32\text{x}10^{-5}$	$5.67\text{x}10^{-5}$
Cut 4	$5.97\text{x}10^{-2}$	$1.08\text{x}10^{4}$	1.18	2.14	$3.91\text{x}10^{-5}$	$3.89\text{x}10^{-5}$
Cut 8	$5.97\text{x}10^{-2}$	$1.08\text{x}10^{4}$	0.966	4.60	$4.60\text{x}10^{-5}$	$4.66\text{x}10^{-5}$

** Activity determined from clean feed reactions **before** Cut 2 Reaction

From Table 4.7, it can be seen that the values of K_I determined from the 3000 ppm nitrogen concentration (Table 4.5 above) can be used to predict the 2000 ppm reactions extremely well. Both Cut 4 and Cut 8 experimental quinoline concentration after reaction almost exactly matched the predicted values. Figure 4.14 shows the predicted and actual average quinoline reaction rate. The error bars on the experimental values represent the 95% confidence limits on the experimental results. The error bars on the predicted concentrations are due to the potential range of K_I as shown in Table 4.6 above. This close prediction, indicates that these two cuts exhibit the expected LHHW inhibition, which makes the inhibition effect dependent on the concentration of the cut.

The inhibition effects of Cut 2 (as determined by using the deactivated catalyst activity of 0.769) is much more severe than the 3000 ppm study K_I value would suggest should be observed. The inhibition displayed by Cut 2 is much higher than either Cut 4 or Cut 8. The final concentration prediction using the 3000 ppm K_I values over estimates the reaction rate significantly, suggesting that Cut 2 does not exhibit the expected LHHW inhibition, and the inhibition may not be dependent on the concentration of the cut. If the concentration of Cut 2 is not important, the term $K_I I$ in Equation 4.3 may be a constant, and Cut 2 may display the same inhibitory effect independent from the concentration of Cut 2. From the 3000 ppm study, the value of $K_I I$ was 1.27 (dimensionless). Using $K_I I$ as a constant, the predicted 2000 ppm average quinoline reaction rate would be 7.85×10^{-7} mol Q / min, which is very close to the experimentally determined

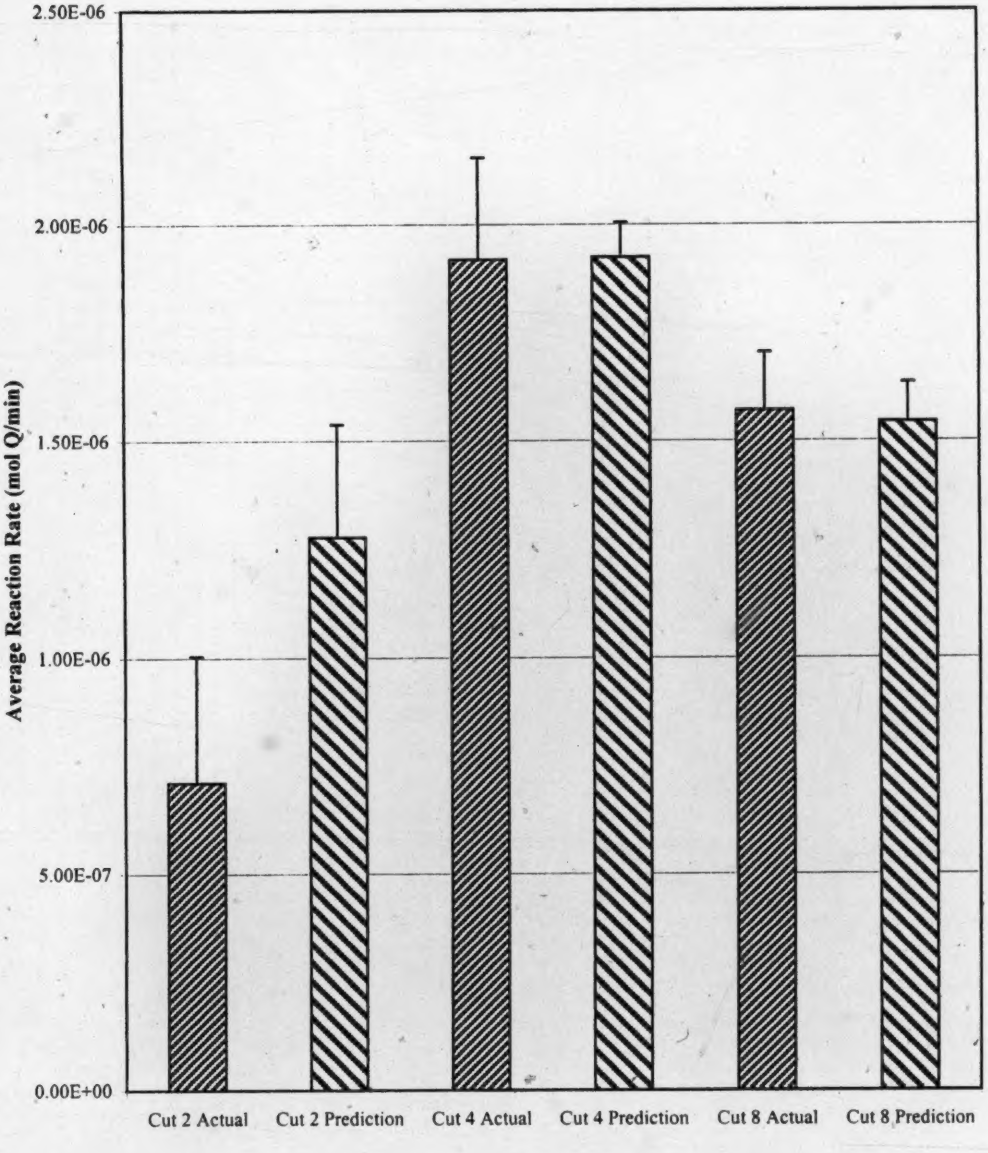


Figure 4.14: Actual and Predicted Average Quinoline Reaction Rate (2000 ppm Nitrogen)

average quinoline reaction rate of 7.02×10^{-7} mol Q / min. At these concentrations of Cut 2, the inhibition effect does not exhibit LHHW inhibition, it shows nearly constant inhibition independent from the concentration. It is possible that at lower concentrations of Cut 2 the effect does follow LHHW inhibition, but this possibility was not investigated. The non-LHHW behavior of Cut 2 is significant and requires further investigation.

The activity of the catalyst before Cut 2 was introduced was 0.966, however, after the Cut 2 reactions, the activity was reduced to 0.769. This is a 20.4 % decrease in catalyst activity, and is much less than the 47.9 % deactivation noticed during the 3000 ppm total nitrogen study. Further experimentation of Cut 2 may determine that below a certain concentration of Cut 2, the catalyst may not be deactivated.

4.5.3 Kinetic Analysis of Inhibition by Narrow Cuts of Gas Oil at Different Temperatures

The Cut 4 and Cut 8 extracts were examined at 330 °C, 350 °C, and 380 °C. Equation 4.5 applies to all temperatures, however, the values of k, K, and K_I may depend on temperature. Since K and K_I are adsorption parameters, the effect of temperature on these constants should be much less than the effects on the rate constant, k. Because the activities of the 330 °C and 350 °C catalysts were not directly compared to the baseline activity of the 380 °C catalyst, it was decided to lump k and a and treat the two as a combined constant (k a). The clean feed reactions run after each cut were used to determine the product of the reaction rate constant and activity of the catalyst (k a) for the reactions with the cut. The determination of "k a" was done numerically in the same fashion as 'a' was determined in Section 4.5.2. Table 4.8 details the components of Equation 4.5. Figure 4.15 shows the same results graphically but also includes the 95 % confidence levels of the experimental values as well as the effect of the 95 % limits on determining K_I (values of K_I from Table 4.6 above). Table 4.8 and Figure 4.15 both show that at 330 °C, the prediction falls close to the observed values, however, for 350 °C, the prediction does not closely resemble the experimental results. The inability to predict inhibition at different temperatures suggests that the adsorption (inhibition) constants (K and K_I) are also temperature dependent, and the dependence is significant.

Table 4.8: Cut Inhibition Kinetics at Varying Temperatures

Cut	Temp (°C)	K	k a	K_I (g feed/g Cut)	Actual C_t (mol Q/g feed)	Predicted C_t (mol Q/g feed)
Cut 4	330	$1.08\text{x}10^{4}$	0.03790	2.14	$5.60\text{x}10^{-5}$	$5.94\text{x}10^{-5}$
Cut 4	350	$1.08\text{x}10^{4}$	0.05717	2.14	$5.04\text{x}10^{-5}$	$5.92\text{x}10^{-5}$
Cut 8	330	$1.08\text{x}10^{4}$	0.03703	4.60	$6.00\text{x}10^{-5}$	$6.54\text{x}10^{-5}$
Cut 8	350	$1.08\text{x}10^{4}$	0.04054	4.60	$5.94\text{x}10^{-5}$	$6.84\text{x}10^{-5}$

The value of "k a" should be reliable as it was determined for each new temperature (and catalyst), and should be constant like both the rate constant and activity were individually constant for the 380 °C kinetics shown above. An assumption was made that the activity, a, was near unity for both the 330 °C and

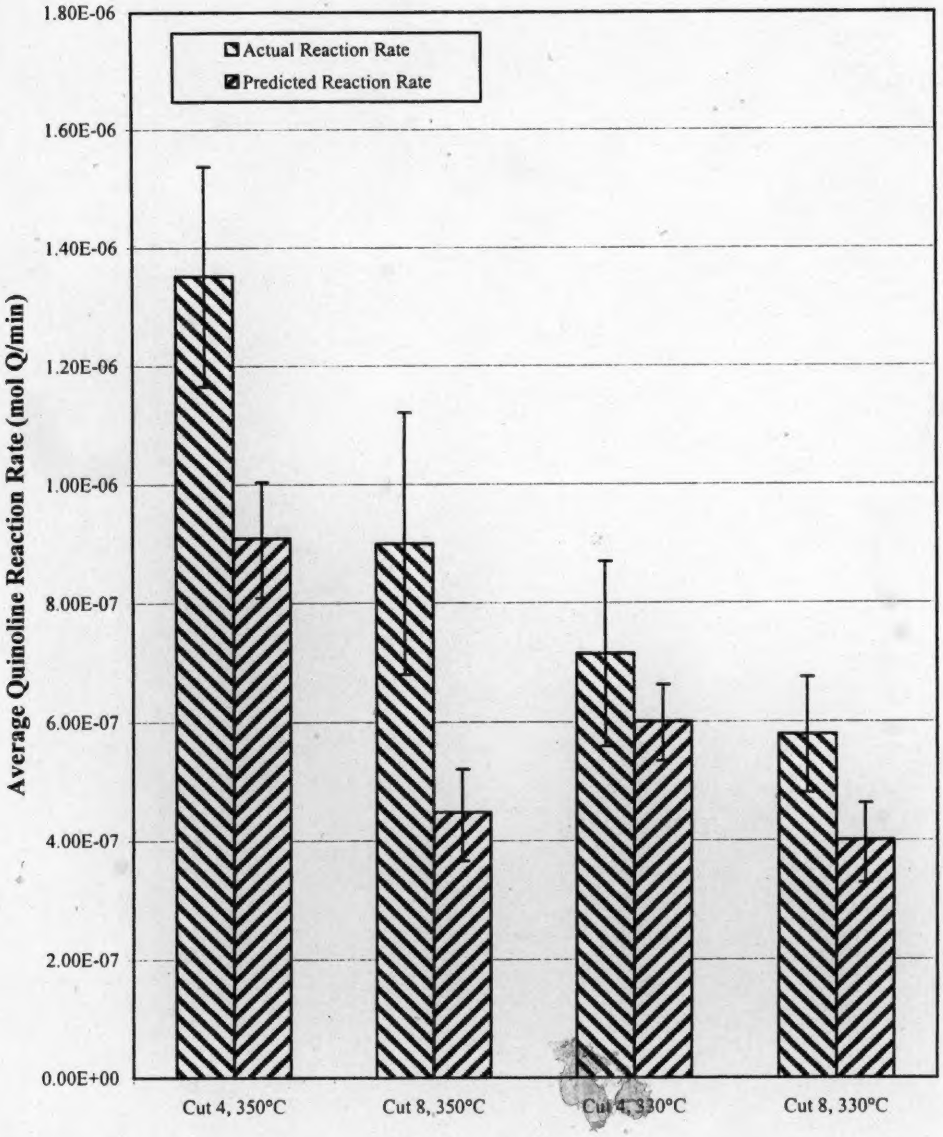


Figure 4.15: Actual and Predicted Average Quinoline Reaction Rate (330 C° and 350 °C)

350 °C catalysts, so the values of k could be approximated as equal to the value of 'k a'. From the data, the value of k was about 0.037 for 330 °C and 0.057 for 350 °C, compared to the value of k determined as 0.060 for 380 °C (Section 4.5). Figure 4.16 shows the relation between the natural logarithm of k as a function of the inverse of temperature. The Arrhenius relationship (Equation 4.8) between k and temperature appears to be generally applicable, however, due to the assumption of values for the activities of the lower temperature catalyst, the fit cannot be certain. The slope of the points in Figure 4.16 gives an estimate for the activation energy of quinoline conversion as 7 kcal/mol Q. This activation energy is low compared to the activation for quinoline HDN of 31 kcal/mol Q as determined by Gultekin et al. (1989). Gultekin et al. (1989) was studying the HDN of quinoline, while this work only examined the conversion of quinoline into some other compound (as opposed to complete HDN). Equation 4.8 shows the Arrhenius relationship between k and the activation energy (Ea), the ideal gas constant (R), a constant (A), and temperature (T) in Kelvin.

$$k = A\exp\left(\frac{-E_a}{RT}\right) \qquad \text{Equation 4.8}$$

4.6 Nitrogen Extracts

To further investigate the apparent inhibition of Cut 4 and Cut 8, the nitrogen rich extracts from the cuts were reacted with quinoline and the catalyst in the batch reactors. The extracts were separated using chromographic methods in order to concentrate the nitrogen species and remove much of the non-nitrogen

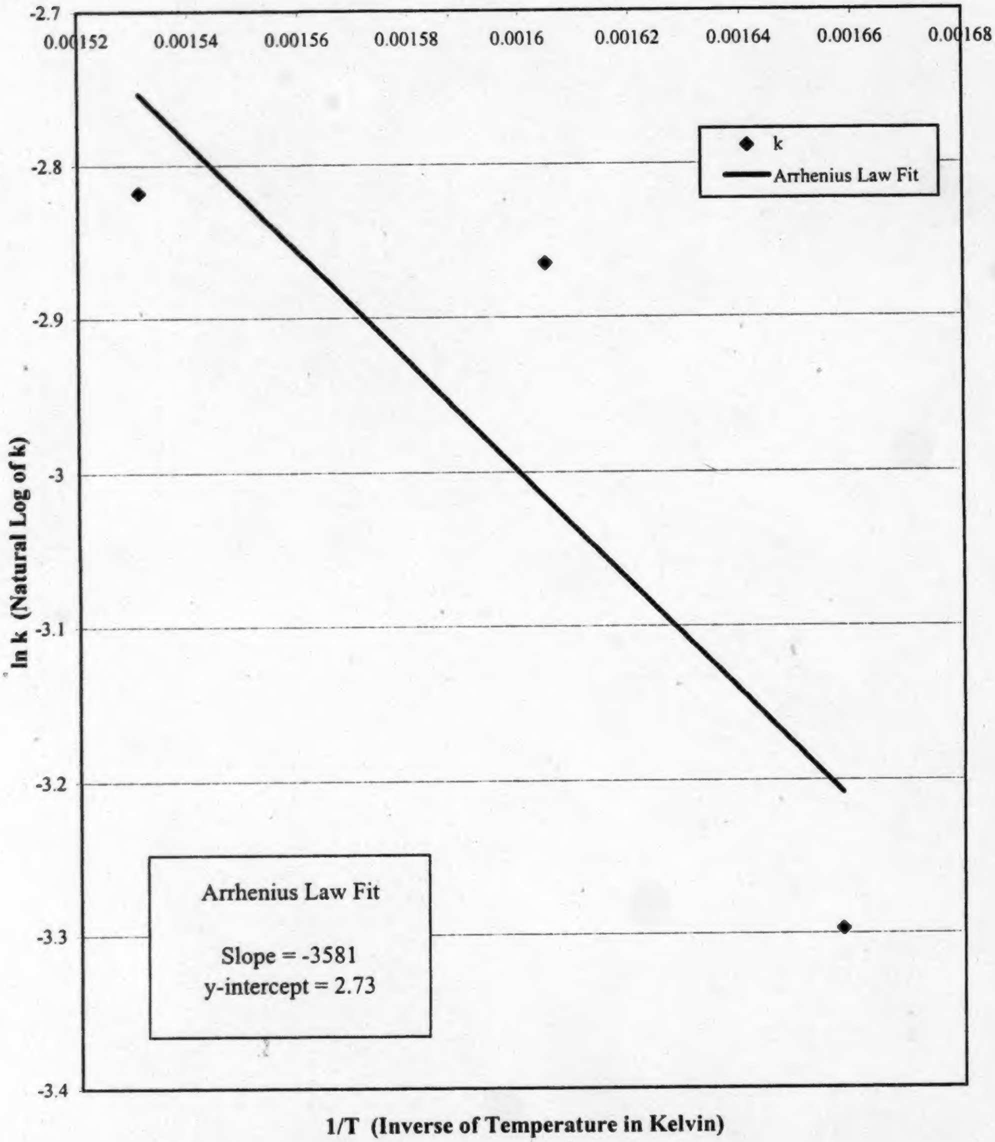


Figure 4.16: Fit of Reaction Rate Contants, k, to Arrhenius Law of Temperature Dependence

species. The extracts were of two types, methanol and methylene chloride extracts. The methanol extract would contain the more polar nitrogen species, while the methylene chloride extract would contain more non-polar species.

4.6.1 Cut 4 Extracts

The nitrogen extracts from Cut 4 were reacted in the reactor system with the same catalyst that had been used for the 3000 ppm total nitrogen Cut 4 and 8 study. This catalyst was selected since the effects of Cut 4 had already been noted on this catalyst, and results obtained from the extract reactions could be compared to the whole cut. Figure 4.17 shows the reaction series and extent of reaction with the Cut 4 extracts.

4.6.1.1 Cut 4 Methylene Chloride Extract

The methylene chloride extract was blended into the carrier gas oil and the extract appeared to dissolve in the carrier oil. The quinoline conversion fell to 20.8 % with the methylene chloride extract in the feed to the reactor. This was a drop of 26.5 % from the clean feed case and 14.2 % below the Cut 4 feed. For the same total nitrogen concentration, the amount of inhibition was higher for the extract.

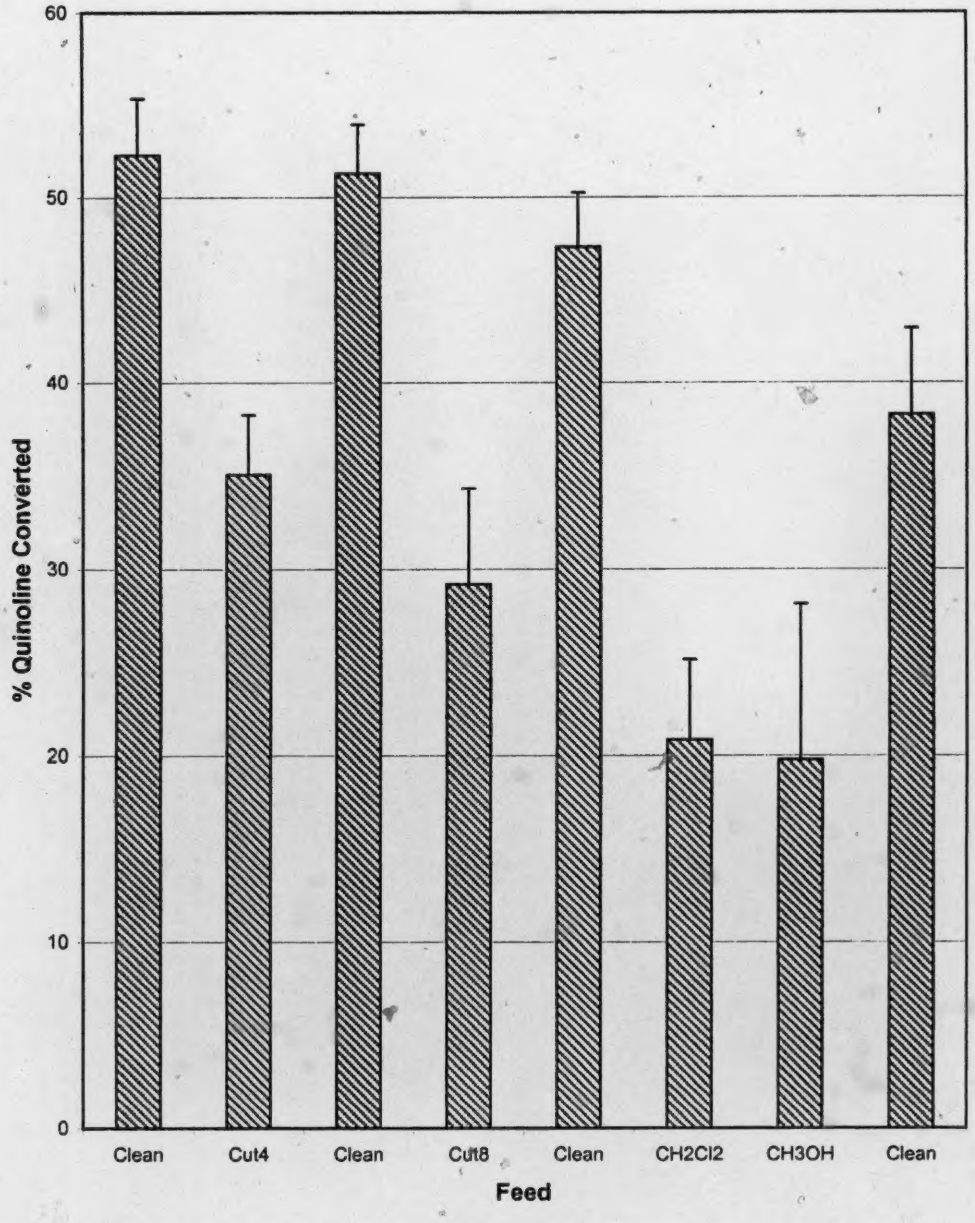
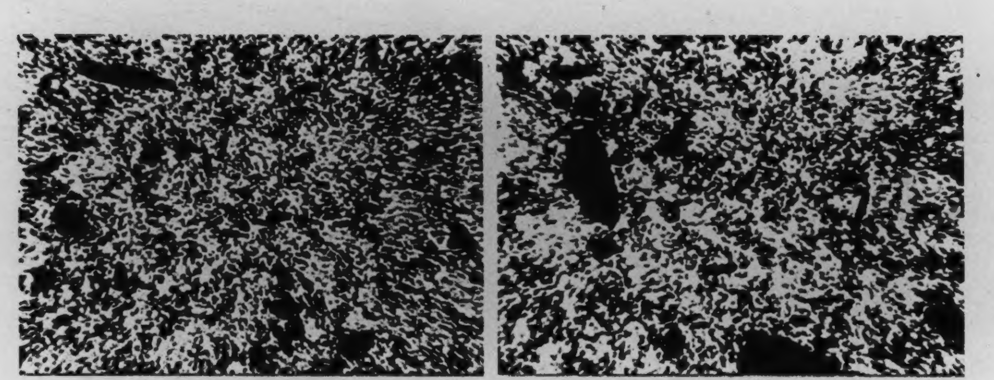


Figure 4.17: Conversion of Quinoline with Nitrogen Extracts from Cut 4 at 380 °C

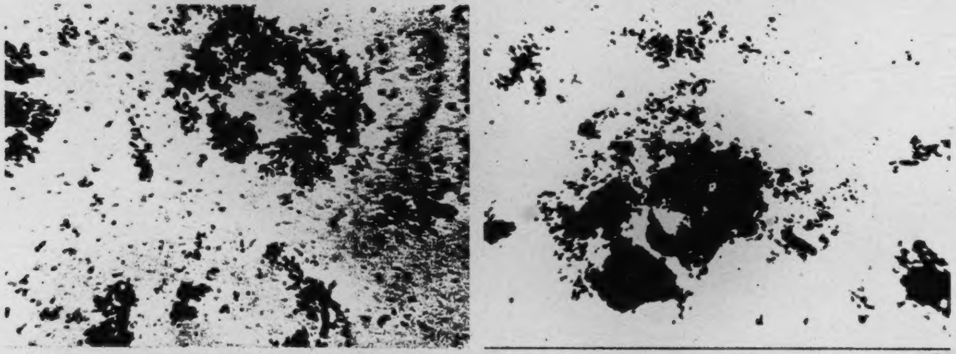
4.6.1.2 Cut 4 Methanol Extract

The methanol extract was blended into the carrier gas oil, but the extract did not completely dissolve at room temperature. Visual observation was able to determine that some of the extract had dissolved. To dissolve more of the extract, the mixture was heated slightly to around 40 °C, but still about 50 to 75 % of the extract was still in solid form. No further heating was applied to the sample, in order to prevent oxygenation or decomposition of the compounds in the carrier gas oil or the extract. The mixture was mixed well and then added to the reactor as a mixture of solid particles suspended in the liquid. After reaction, solid particles were noted in the product oil. The particles were examined using an optical microscope in order to discover if the particles appeared to have undergone some sort of physical transformation. Figures 4.18(a) to 4.18(f) compare six different pictures between the feed and product solids. The product solids appear to be composed of flocs of many smaller particles as opposed to the feed solids which were made of larger particles with sharper more defined edges. The difference in the feed and product solids suggests that there was some dissolution during the reaction process. Although it cannot be proven, the microscope results suggest that the extract dissolved at reaction temperature and then reprecipitated as the reactor cooled off.

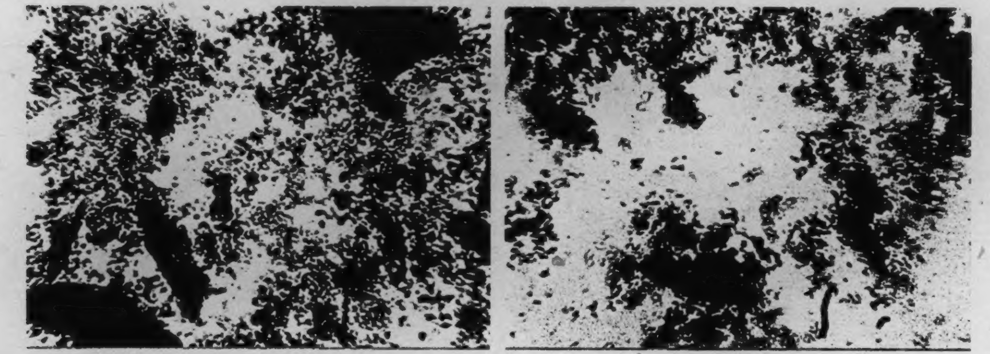
The methanol extract was added to the catalyst reaction system immediately after the methylene chloride extract. Because there was only enough methanol extract available to conduct three experiments, it was decided to react the extract



a) & b) Feed Solids at 12.5x Magnification (field of view 1280 by 940 μm)



c) & d) Reacted Solids at 12.5x Magnification (field of view 1280 by 940 μm)



e) Feed Solids & f) Reacted Solids at 25x Magnification (field of view 640 by 470 μm)

Figure 4.18: Microscopic Images of Solids from Cut 4 Methanol Extract Before and After Reaction

immediately after the methylene chloride extract. This meant the loss of information regarding the deactivation caused by the methylene chloride extract, but since there could only be three reactions with the methanol extract, starting from an already inhibited state would likely allow observation of inhibition in fewer reaction steps. If the methanol extract was added after clean feed, the three reactions could possibly show a downward trend (transition), with no real way of identifying if the final reaction was near the actual final steady state reaction condition. Starting from the steady state achieved during the methylene chloride extract reactions would show if the methanol extract was more or less inhibitory and the approximate difference between the two inhibitions. Either way, the evidence would not be strong enough to conclude the final steady state inhibition of the catalyst by the methanol extract, but with the addition following the methylene chloride extract, it can be noted whether the methanol extract was more or less inhibitory than the methylene chloride extract.

The three reactions with the methanol extract were all very close to the average of the methylene chloride extract reactions, with an average of 19.8 % quinoline conversion and a range from 17.6 to 22.9 %. The large 95 % confidence limits are the result of the small number of reactions (only three reactions). There was perhaps slight evidence of an increase in conversion as the three reactions sequentially increased, but this increase was small compared to the error in the reaction system. If the steady state inhibition of the catalyst caused by the methanol extract was going to be much less than the methylene chloride extract, the increase would have been much larger, since transitions were generally quite rapid for these high temperature experiments. Since there was little evidence of a prolonged transition from one extract to the other the conclusion is that the methylene chloride and methanol extracts had similar effects on the inhibition of the catalyst at a constant total concentration of nitrogen compounds.

4.6.1.3 Clean Feed After Cut 4 Extracts

After the two Cut 4 nitrogen extracts were reacted with the catalyst, clean feed was reintroduced to the system. The activity increased to 38.3 % quinoline conversion, which was a drop of 9.0 % of the pre-extract clean feed conversion. Since the two extracts were fed to the system in series without a clean feed reaction set between the two extracts, the deactivation cannot be attributed to both or either one of the extracts individually. This apparent deactivation was unexpected since the whole Cut 4 feed did not exhibited any deactivation, but the reaction series with the two nitrogen extracts did exhibit a significant level of inhibition. Although the total nitrogen concentration was the same due to Cut 4 or each of the individual extracts, each nitrogen component (i.e. each polar and non-polar compound) was present in a much higher concentration at any one time with the extracts than was present in the entire Cut 4. The higher concentrations of each nitrogen species during the extract reactions may explain the deactivation of the catalyst.

4.6.2 Cut 8 Extracts

A new batch of catalyst was used to start the Cut 8 extract study since the catalyst batch in the Cut 4 extract study had been deactivated during the previous experiments. The reaction series of this catalyst with the Cut 8 extracts is shown in Figure 4.19. The new catalyst was reacted with clean feed to obtain a baseline at 54.1 % of quinoline converted. Cut 8 was then added in order to compare the Cut 8 extract information with the Cut 8 feed as a whole. The amount of quinoline reacted dropped to 24.9 % with the Cut 8 and then recovered to 56.2 % when the clean feed was reintroduced.

4.6.2.1 Cut 8 Methylene Chloride Extracts

The methylene chloride extract was added as a solid to the reactor and was not mixed with the carrier gas oil like the Cut 4 extracts were. The amount of quinoline conversion was drastically increased, to the point where the amount of quinoline left was below the detection abilities of the GC with the carrier oil background, suggesting greater than 90 % of the quinoline reacted. Also noted during these reactions was the generation of a large amount of black powder that was left as a residue on the walls of the reactor and in the product oil. Each reaction with the extract produced a thick coat of the black powder on the walls of the reactor, which was cleaned thoroughly between these reactions in order to remove as much of the powder as possible. An estimated 2-5 mg of powder was produced during each reaction with the methylene chloride extract. The amount of this black

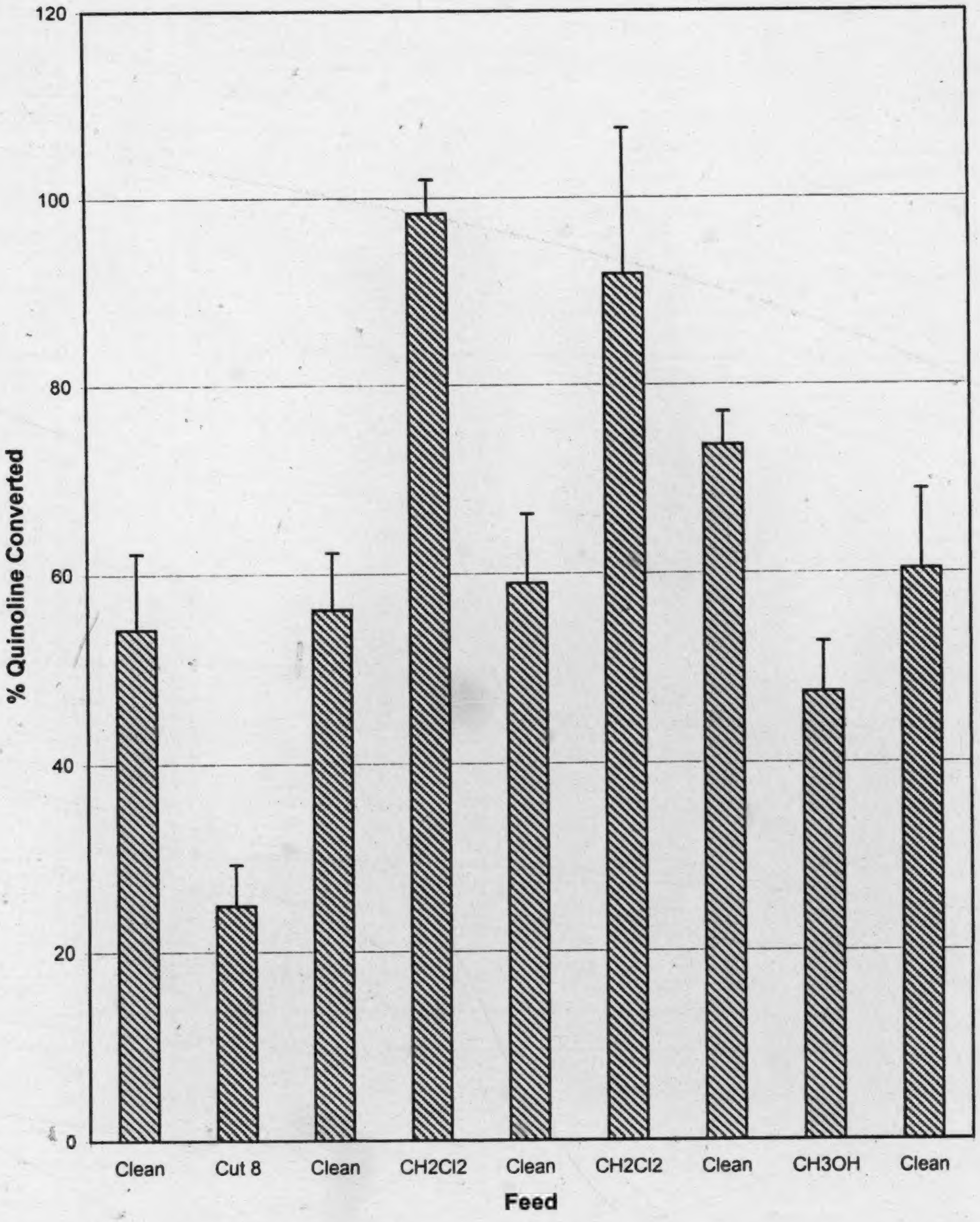


Figure 4.19: Conversion of Quinoline with Nitrogen Extracts from Cut 8 at 380 °C

powder was much more prevalent than the small dusting that had been observed in the reactors during the other portions of this work.

When the clean feed was reintroduced to the catalyst, the amount of quinoline reacted returned to the original amount of 59.0 %, however, the last reaction of the set was completed in a new reactor since the previous one had been increasingly hard to seal. During the next set of reactions, still with clean feed, it was noticed that all five reactions that were conducted in the new reactor had on average 29.5 % less quinoline converted than the reactor that had been exposed to the methylene chloride extract. At the time this led to the belief that the new reactor was one of the occasional faulty reactors that would have a lower extent of reaction than the other reactors (as explained in Section 4.1.4).

Because of this belief that the new reactor was faulty, two new reactors were selected and another run of the methylene chloride extract reactions was started in order to verify the increased activity with the extract, without checking the new reactors with the clean feed first. Once again the amount of quinoline reacted exceeded the ability of the GC to measure the residual quinoline (more than 90 % reacted). Once again a large amount of black solids were generated. Clean feed was reintroduced and the amount of quinoline reacted fell to 73.6 % and remained stable at this new value, suggesting the catalyst activity had been permanently enhanced.

The black solids were collected and analyzed by Energy Dispersive X-ray (EDX) on a Scanning Electron Microscope within the Chemical Engineering

Department and also sent to the University of Alberta Chemistry Department for analysis on the carbon, sulfur, nitrogen, and hydrogen content of the solids. The EDX could not analyze for carbon, but could detect metals, sulfur, and chlorine. Table 4.9 shows the results of the EDX analysis.

Table 4.9: EDX Analysis of Reactor Solids

Element	Atomic %
S	43.34
Cl	3.06
Fe	37.25
Cr	10.39
Ni	4.03
Cu	0.82
Al	0.73
Si	0.35

Since the amount of carbon could not be measured using EDX, the Department of Chemistry analyzed the sample in order to estimate the amounts of carbon, hydrogen, sulfur and nitrogen. This second analysis would confirm that the metals shown by EDX were not just a very small fraction of the sample in a predominantly carbon deposit. The elemental analysis showed that there was 5.62 mol % C, 0.45 mol % H, and 0.35 mol % N. Sulfur composed 12.6 mol % of the sample. This confirmed that the sample was mainly a metal sulfide deposit and not a carbon-based deposit.

Using the amount of sulfur in the two analyses to try and normalize the amount of each atom in the sample did not yield 100 % of the mass of the sample. This discrepancy was because the elemental analysis which returned the 12.6 mol %

sulfur is unable to determine the amount of sulfur correctly when the sulfur is present as a metal sulfide and not an organic molecule.

These analyses confirmed the deposit to be metal sulfides and not coke or other carbon based deposits or precipitates. The effects of these sulfides were not thought to be significant at the time because of the small amounts of surface area and mass compared to the much higher catalyst surface area and mass. The following section details the significant effects of these metal sulfide solids.

4.6.2.2 Cut 8 Methanol Extracts

The methanol extract was added to the reactor as a solid. The same two reactors were still being used from the previous methylene chloride extract series above. The amount of quinoline converted dropped to 47.4 % with the methanol extract from the clean feed conversion of 73.6 %.

Two new reactors were selected and used with one old reactor when the clean feed was reintroduced to the catalyst. The amount of quinoline reacted dropped to an average of 30.1 % with the two new reactors and increased to 59.5 % with the old reactor. The connection between the previous new reactor exhibiting low activities (in Section 4.6.2.1) with clean feed and these two new reactors exhibiting low activity with clean feed made the original belief that the first reactor was faulty unlikely. Now three different new reactors were showing differences from old reactors that had been exposed to the methylene chloride extract, suggesting that the new reactors were not faulty and showing low activity, but some other phenomenon was causing an artificially high activity in the old reactors.

The one old reactor that had just been removed from service was recommissioned and six reactions were conducted with the two reactors that had been exposed to the methylene chloride extract. The first four reactions used the catalyst and showed on average 60.8 % quinoline conversion with clean feed. The last two reactions were conducted without catalyst, so only clean feed, CS_2, and H_2 was added to the reactors. Without the catalyst, the amount of quinoline converted was 41.8 % and 61.4 % for the two reactors showing that the methylene chloride extract had caused the reactors to have a very high residual activity on the walls of the reactors. This explained the low activity in the new reactors that had been unexposed to the methylene chloride extract since they would have unreactive walls. This result makes the data from the reaction series with the Cut 8 extracts highly suspect, as the reactor wall effects became predominant over catalyst activity. With this information two observations can still be noted.

1) With the new reactor, the amount of quinoline reacted after the first methylene chloride extract series was 29.5 % showing that significant deactivation had occurred to the catalyst.
2) The methanol extract inhibited the quinoline reactions. This may have been an effect on just the catalyst, just the reactor walls, or a combination effect on the reactor walls and the catalyst.

The methylene chloride extract was analyzed to identify if any methylene chloride had carried over from the extract separation techniques. Chlorine was suspected because of the possibility it could be in the feed, the corrosion damage to the stainless steel reactors, the damage and deactivation to the catalyst, and the level of chlorine shown (3.6 mol%) in the EDX analysis of the black powder generated during the methylene chloride extract reactions. A sample of the extract was sent for Nuclear Magnetic Resonance (NMR) at the University of Alberta Department of Chemistry. A peak matching the chemical shift for methylene chloride was noted. The amount of methylene chloride in the extract was found to be 23300 ppm. This concentration of methylene chloride corresponds to a 433 ppm level of chlorine in the reactor.

The catalytic activity of the reactor walls was attributed to the results of the attack by chlorine in the extract, but the very high activity with such a relatively small surface area could not be explained. The 4.03×10^{-3} m^2 area of the reactor wall was as reactive as the 0.14 g of new catalyst with a minimum of 22.4 m^2 of surface area, based on the manufacture's minimum surface area value of 160 m^2/g catalyst)

4.7 Conversion of Quinoline Intermediates

Decahydroquinoline (DHQ) was chosen as a compound to study the effect of the cuts on the conversion of quinoline intermediates. DHQ is a fully hydrogenated compound and was selected in order to determine if the cuts were affecting the hydrogenation reactions, the ring cracking hydrogenolysis reactions, or both. The DHQ used in this work was a mixture of cis and trans DHQ.

4.7.1 Method for Decahydroquinoline

The DHQ work was completed with clean feed and Cut 8 and showed promise as an area of further study since the methods used in this work appear to lend themselves to the DHQ work as well. The temperature of the inlet in the GC was reduced to 230 °C as it was found that at the inlet temperature of 300 °C for the quinoline work decomposed the DHQ and gave small peaks. Once the inlet temperature was reduced, the peaks size for decahydroquinoline increased. Due to the placement of the DHQ peaks, a higher extent of reaction could be accurately measured.

To ensure that the DHQ was stable at reactor conditions and that a significant amount of DHQ was not lost during feed preparation, reactor loading, and product handling, a reaction with DHQ feed and no catalyst was performed. The reaction without catalyst was analyzed and it was found that 8.3 % of the feed DHQ was lost in the reactor loading, reaction, and product recovery steps. This amount was larger than the amount of quinoline that disappeared during the reaction without catalyst, but was much smaller than the amount of DHQ that reacted when catalyst was present.

4.7.2 Clean Feed Reactions with DHQ

The reactions with DHQ and clean feed at a temperature of 380 °C and 20 minutes, had an average of 84.1 % conversion. The range was very small, with all of the reactions falling between 82.5 and 84.8 % conversion.

4.7.3 Cut 8 Reactions with DHQ

Cut 8 was introduced and the GC peaks for decahydroquinoline disappeared, suggesting 100 % conversion, however, two new peaks at later retention times were noted. In order to determine what these two new peaks were, a mixture of 1 % DHQ and n-hexadecane was reacted with the catalyst for 10 minutes and 8 minutes and the resulting product analyzed in the GC. The cis and trans DHQ peaks were present, but so were three large peaks at later retention times, including the two times noted during the Cut 8 reactions. Figure 4.20 shows the GC curve for the hexadecane reactions. GC-MS on the sample showed that the larger of the two DHQ peaks was trans-decahydroquinoline. The largest of the three product peaks was 5,6,7,8-tetrahydroquinoline (THQ) and the two other smaller peaks had similar spectra to 5,6,7,8-THQ, but positive identification could not be made. Figure 4.21 shows the reaction network for quinoline hydrodenitrogenation as proposed by Satterfield and Yang (1984). The smaller peaks could not be 1,2,3,4-THQ as the retention times did not match the known retention times of 1,2,3,4-THQ from the authentic standard.

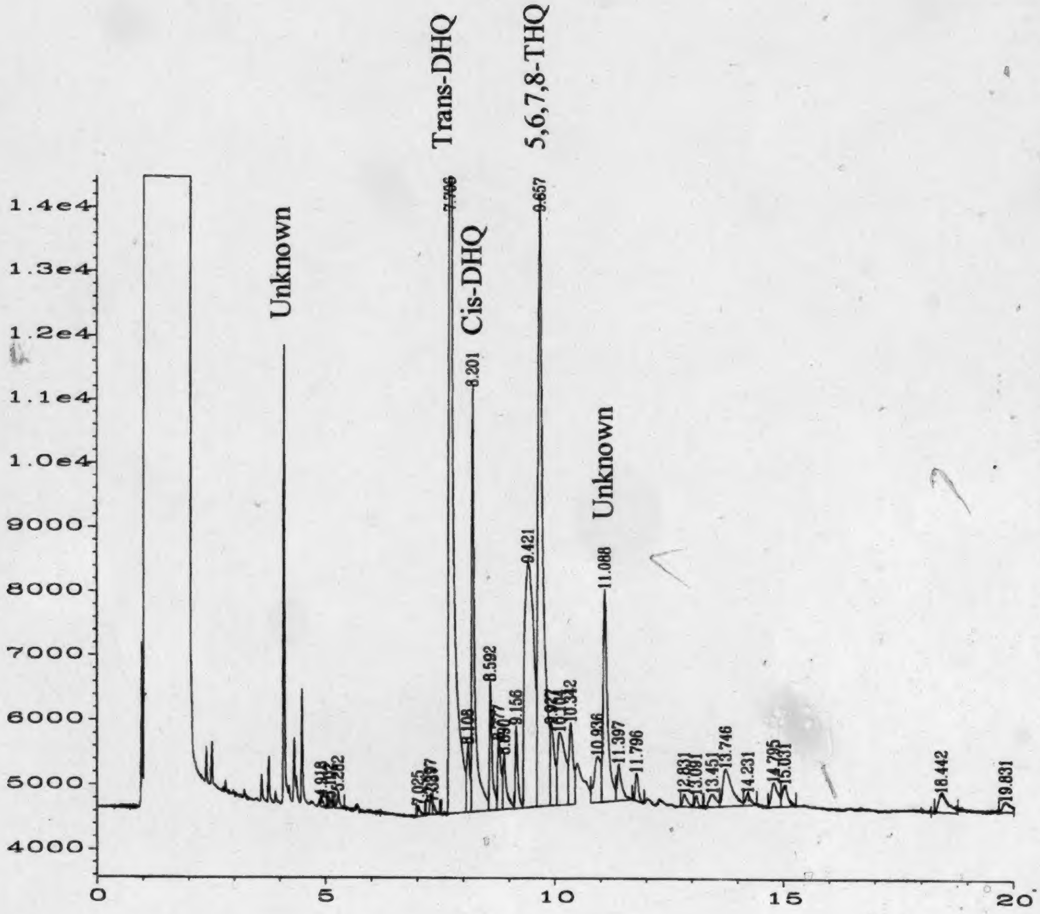


Figure 4.20: Portion of GC Curve from DHQ and Tetralin Reactions

Since there was no calibration with 5,6,7,8-THQ, the amount of the compound produced can only be estimated. Using the same calibration factor as the decahydroquinoline, roughly 0.39 % of the product oil was 5,6,7,8-THQ. This means that 42.4 % of the decahydroquinoline reacted to form 5,6,7,8-THQ. This result does not take into account the smaller peak which could not be identified. The second peak was half of the size of the larger 5,6,7,8-Tetrahydroquinoline peak and may have accounted for another 20 % of the feed DHQ. This suggests that perhaps as little as 40 % of the DHQ may have undergone complete HDN compared to the approximately 84 % that hydrodenitrogenated in the clean feed reactions. Since the clean feed DHQ reactions did not have any large product peaks, most of the DHQ was converted into smaller compounds that eluted with the solvent, suggesting at that as a minimum, the nitrogen ring was likely broken, and perhaps the nitrogen was removed. The Cut 8 reactions left heavy nitrogen containing species behind, suggesting that the rings had not been broken.

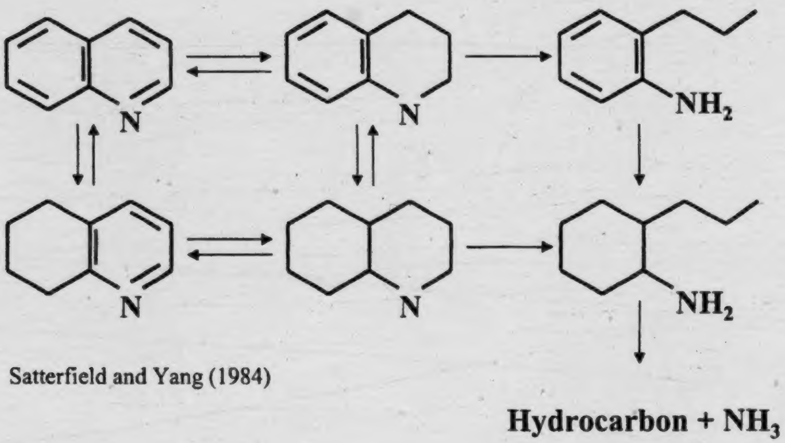

N
N
NH₂
N
N
NH₂
Satterfield and Yang (1984)
Hydrocarbon + NH₃

Figure 4.21: Simplified Reaction Network for Quinoline (Satterfield and Yang, 1984)

5 Discussion

5.1 Inhibition of Quinoline Conversion

All of the cuts and extracts showed lower quinoline conversion than the experiments with clean feed. The lower conversion level suggests that all of the cuts had an inhibitory effect on quinoline conversion. The total nitrogen concentration of the reactions with the cuts and extracts was higher than the clean feed (quinoline and carrier gas oil only) reactions. The presence of nitrogen compounds may reduce the amount of quinoline converted. However, it is important to note that even at the same total nitrogen concentration, each of the cuts exhibited different levels of inhibition.

5.1.1 Inhibition of Quinoline due to Gas Oil Cuts

The amount of inhibition displayed by each cut was different (at the same total nitrogen concentration), showing that the inhibition is not simply a function of total nitrogen content. Cut 8 showed a higher level of inhibition than Cut 4 at all three temperatures (as shown in Figures 4.7, 4.8, and 4.9). Cut 8 also showed a higher level of inhibition than Cut 4 when the concentration of the cuts were reduced to half of the standard level at the 380 °C reaction temperature (Figure 4.11). This agrees with the hypothesis that polyaromatic and higher molecular weight compounds absorb to the catalyst preferentially and inhibit quinoline reaction rates.

Since Cut 2 was the lightest cut studied, it was expected that it would affect the catalyst the least. Cut 2 had smaller amounts of the heaviest molecules, polyaromatics, and large, hard to hydrotreat nitrogen compounds to absorb to the catalyst surface. Cut 2 inhibition was expected to be minimal and anticipated to be less than the Cut 4 inhibition. The Cut 2 data, however, does not follow the hypothesis. Cut 2 significantly inhibited quinoline conversion. This inhibition occurred at both the 3000 ppm nitrogen concentration and the 2000 ppm nitrogen concentration at 380 °C. The higher inhibition with Cut 2 could not be due to the polyaromatic or higher molecular weight compounds as Cut 2 should have much less of these large compounds than either Cut 4 or Cut 8. However, since Cut 2 was added at a higher concentration than Cut 4 or Cut 8 (to achieve the same total nitrogen concentration), any inhibitory compounds in Cut 2 would have been present in large amounts. Further study is warranted to identify the cause of the large apparent inhibition.

Kinetic analysis of the three cuts at reaction conditions of 3000 ppm total nitrogen and 380 °C showed the inhibition constants (K_I from Equation 4.4), which helps indicate the cuts relative inhibition. The values of K_I can be found in Table 4.5. The values of K_I determined in the 3000 ppm total nitrogen study were able to predict the Cut 4 and Cut 8 2000 ppm total nitrogen reactions very well (Figure 4.14). This means the inhibition exhibited by the two cuts was consistent with LHHW type kinetics where the amount of inhibition is related to the concentration of the cut only. This relationship to cut concentration can be seen in

Equation 4.3. If K_I for a cut is constant, as LHHW kinetics suggest it should be, the cut concentration influences the inhibition as indicated by Equation 4.3, and the concentration of the cut determines the inhibition. The Cut 2 inhibition constant (K_I) determined from the 3000 ppm nitrogen study could not predict the average quinoline reaction rate during the 2000 ppm study. Unlike Cut 4 and Cut 8, Cut 2 did not follow LHHW type behavior. In Section 4.4.3.2, it is shown that the term $K_I I$ in Equation 4.3, may be a constant for the Cut 2 reactions, indicating that the inhibition exhibited by Cut 2 may be independent of the concentration of Cut 2. It is important to note that the value of K_I was influenced by the amount of deactivation of the catalyst by Cut 2 and may be part of the reason for the non-LHHW kinetics observed. The nearly constant inhibition exhibited by Cut 2 in the 3000 and 2000 ppm nitrogen reactions suggests the inhibition may be the result of a mechanism other than simple adsorption to the catalyst active sites.

The amount of sulfur present in the reactor with Cut 2 was higher than either Cut 4 or Cut 8 as shown in Tables 3.6 and 3.7. The concentration of sulfur in Cut 2 was 41800 and 27000 ppm sulfur for the 3000 and 2000 ppm total nitrogen feeds respectively. At these sulfur levels, if all of the sulfur completely reacted to form H_2S and hydrogen filled the carbon bonds where the sulfur atom was removed, (not counting the hydrogenation of the aromatic rings) the H_2 partial pressure reduction would be approximately equivalent to that resulting from a 109 μL and 41 μL addition of CS_2. Including the actual 30 μL CS_2 added, a total equivalent CS_2 addition of 139 μL and 71 μL of CS_2 would be present for the 3000 and 2000 ppm total nitrogen Cut 2 feeds respectively. The H_2 partial pressure should not play a major role in the amount of quinoline converted due to H_2S formation alone (see Section 4.1.5.1, Figure 4.5).

The lower boiling point of Cut 2 would have resulted in a potentially higher pressure in the reactor, as more of Cut 2 would have volatilized at 380°C than either Cut 4 or Cut 8. The volatilization of Cut 2 would have had the beneficial effect of increasing the concentration of quinoline in the liquid phase, but the detrimental effect of decreasing the hydrogen concentration in the gas phase, although the hydrogen partial pressure would have been unaffected. The reduction in hydrogen concentration in the gas phase may account for the apparent significant inhibition of quinoline conversion by Cut 2.

Another possibility is that there is another class of compounds in the cuts that are not molecular weight or boiling point dependent so they have higher concentrations in Cut 2 (such as easily hydrogenated aromatics) and therefore make Cut 2 more inhibitory than Cut 4 or Cut 8.

5.1.1.1 Temperature Dependence of Inhibition due to Gas Oil Cuts

Both Cut 4 and Cut 8 were studied at 330 °C, 350 °C, and 380 °C. In order to compare the reactions across the three temperatures, the average quinoline reaction rate must be compared. Figure 4.14 shows the quinoline reaction rate at 380 °C with Cut 4 and Cut 8, while Figure 4.15 shows the quinoline reaction rate at 330 °C and 350 °C. When K and K_I are approximated as constant with respect to temperature, the model used to predict the average quinoline reaction rate does not accurately predict the average reaction rate at temperatures below 380 °C. This results indicates that the inhibition displayed by both Cut 4 and Cut 8 are temperature dependent.

5.1.2 Inhibition due to Nitrogen Extracts

Due to the presence and effects of the residual methylene chloride and the resulting chlorine in the Cut 8 methylene chloride extract, it is difficult to make inferences on the relative effects of the Cut 8 extracts compared to Cut 8. The methanol extract was inhibitory, but due to the chlorine damage to the catalyst and the apparent activation of the reactor walls, no relative comparison to the amount of Cut 8 inhibition can be made.

The Cut 4 extracts both exhibited more inhibitory effects than the whole of Cut 4, for the same total nitrogen concentration (Figure 4.17). This information tends to suggest that the nitrogen compounds have a very important effect on the inhibition of quinoline conversion, and the non-nitrogen compounds have no significant inhibitory effects. If the inhibition was due to the other non-nitrogen compounds, the nitrogen extracts would not have exhibited such strong inhibition by themselves. Since both the methylene chloride and methanol extracts exhibited the same amount of inhibition, the different types of nitrogen compounds that may be in the different extracts do not seem to be of significant importance.

5.2 Deactivation of Quinoline Conversion

Because the reactions were performed as discreet batch reactions, noting and quantifying deactivation is harder to monitor than for a continuous flow reactor, however a few items can be stated.

5.2.1 Deactivation due to Cut 4, Cut 8, and their Extracts

The catalysts did not display any consistent indications of deactivation after their exposure to Cut 4. None of the reactions at any of the temperatures showed any signs of deactivation after Cut 4.

Cut 8 appeared to deactivate two of the catalyst batches however, one of the apparent deactivations came after the addition of CS_2 was forgotten for one of the 330 °C Cut 8 reactions. The lack of CS_2 in the reactor for the Cut 8 reaction had an immediate effect that persisted. The apparent deactivation of the catalyst is believed to be a result of the lack of CS_2 in the one reaction. Other reactions at 330 °C did not show deactivation after the Cut 8 reactions. The other apparent deactivation by Cut 8 occurred during the 350 °C reactions. Although this deactivation cannot be explained by experimental error, it was the only non-explainable deactivation that occurred with Cut 8 and is believed to be an anomaly.

The Cut 8 methylene chloride extract deactivated the catalyst as shown by the clean feed reactions decreasing from 56.2 to 29.5 % quinoline conversion. However, as explained earlier in the previous chapter, Section 4.6.2.1, the presence of chlorine in the extract resulted in damage to the catalyst. The deactivation cannot be attributed to the compounds in the extract. An interesting result of the chlorine in the reaction system is that even though the catalyst was damaged and deactivated, the conversion of quinoline increased. The reactor walls became 'activated' and accounted for a large portion of the quinoline conversion, 41.8 % and 61.4 % quinoline conversion in two reactions performed without catalyst.

5.2.2 Deactivation due to Cut 2

Cut 2 showed deactivation in both of the reaction sets that it was used in. Both reaction sets were at 380 °C and other temperatures were not examined. In both the 3000 ppm and 2000 ppm nitrogen reactions, Cut 2 exhibited more severe inhibition than either Cut 4 or Cut 8. The inhibition persisted after Cut 2 was removed, suggesting that permanent deactivation had occurred. During the 3000 ppm nitrogen study, the reactions with clean feed were continued for 12 reactions after Cut 2 was removed and the clean feed quinoline conversion only returned to 28.9 % quinoline conversion compared to the starting 50.4 % quinoline conversion before Cut 2 was introduced to the catalyst. During the 2000 ppm nitrogen study, after the Cut 2 reactions, the quinoline conversion recovered to 43.4 %, down from the 52.1 % quinoline conversion before the Cut 2 reactions.

Kinetic analysis in Section 4.5.1 showed that for the experiments with 3000 ppm total nitrogen, the activity decreased from 0.924 to 0.481 (a 47.9 % reduction). Kinetic analysis in Section 4.5.2 showed that for the 2000 ppm total nitrogen reactions, the activity decreased from 0.966 to 0.769 (a 20.4 % reduction).

These two sets of reactions showed that the deactivation seemed to be dependent on the Cut 2 concentration as the higher concentration reactions resulted in higher deactivation.

Although the Cut 2 inhibition discussed earlier in Section 5.1.1 could potentially be explained by hydrogen partial pressure reduction due to the higher sulfur concentration in the Cut 2 experiments, the apparent deactivation cannot. If the Cut 2 reactions had been inhibited by H_2 partial pressure reduction, once the clean feed was reintroduced to the catalyst, the amount of quinoline converted should have returned to the previous clean feed levels. The hypothesis of this work suggested that the increased polyaromatics and molecular weight compounds could result in permanent adsorption to the catalyst and hence deactivation. However since Cut 2 has less of these compounds, there must have been a class of chemical compounds that are present in Cut 2 that caused the deactivation. Since deactivation was not noted in Cut 4 or Cut 8, these compounds are not concentrated in the higher boiling fractions of the coker gas oil and must be attributed to some factor other than molecular weight or aromaticity. This result suggests that utilizing an alternative method of separation that does not separate the coker gas oil by distillation may be beneficial. This separation may be able to help identify what is present in Cut 2 in high concentrations that accounts for the catalyst deactivation, but is not present in Cut 4 or Cut 8 to the same extent. Further study with the Cut 2 nitrogen extracts could possibly provide additional information.

5.3 Reaction Rate Constant Dependence on Temperature

The average reaction rate of quinoline was examined as a function of temperature. Assumptions on the catalyst activity had to be made in order to determine the reaction rate constant at 330 °C and 350 °C, since the rate constant was not examined at each temperature. The rate constant appeared to somewhat follow Arrhenius theory for temperature dependence (Figure 4.16), and an activation energy of 7 kcal/mol Q could be estimated.

5.4 Quinoline Derivative Study

During the clean feed reactions, 84.1 % of the DHQ was converted to light or untraceable compounds. Once Cut 8 was added to the reactions, the amount of DHQ remaining after reaction was not measurable using the techniques of this work. However, a large amount of 5,6,7,8-THQ was generated. Preferential adsorption of either 5,6,7,8-THQ or DHQ to the catalyst is not suspected as a cause of this result since LaVopa and Satterfield (1988b) show that the two compounds have the same adsorption constant.

One possible explanation is that Cut 8 inhibited the hydrogenation reactions. With slower hydrogenation, any 5,6,7,8-THQ that formed took much longer to hydrogenate back into DHQ (essentially became the rate limiting reaction). With carbon-nitrogen hydrogenolysis (ring opening) reactions uninhibited or less severely inhibited, nearly all DHQ formed that formed from 5,6,7,8-THQ hydrogenation had an aromatic ring opened and was no longer DHQ. This explains why there was a large amount of 5,6,7,8-THQ remaining after reaction with less than detectable amounts of DHQ. However, if hydrogenation was inhibited to such an extent, it is difficult to explain how dehydrogenation of the DHQ occurred. If inhibitors adsorbed to the catalyst sites, dehydrogenation should be inhibited as well as hydrogenation, since they both require catalyst sites. Also, according to Satterfield and Yang (1984) the dehydrogenation of DHQ to 5,6,7,8-THQ is roughly 5 times slower than the hydrogenation of 5,6,7,8-THQ to DHQ, causing further concern as to how the 5,6,7,8-THQ was created in the first place.

Since there was no evidence of the 5,6,7,8-THQ peaks or other large molecular weight quinoline byproducts during the clean feed reactions, the DHQ must have undergone HDN and became smaller lighter molecules that the GC did not detect in significant quantities, or were hidden in solvent and other lighter peaks. When Cut 8 was present in the reactor, a large concentration of nitrogen containing DHQ byproducts remained. Cut 8 is therefore suspected to inhibit the HDN of decahydroquinoline.

Since this limited work cannot support a conclusion to explain the behavior of Cut 8 on DHQ reactions, further study may provide information as to how Cut 8 influences the DHQ/5,6,7,8-THQ reactions.

6 Conclusions

6.1 Inhibition

All nitrogen containing fractions and extracts displayed some level of inhibition on quinoline conversion. The amount of inhibition was not the same for different feeds with the same total nitrogen concentration. This means that nitrogen content alone is not the only factor that caused the inhibition, and some consideration for the size and type of the nitrogen molecules and other non-nitrogen species must also be given.

Cut 8 displayed more inhibition than Cut 4 per mass of cut (or per mass of nitrogen). This result suggests that molecular weight of the nitrogen compounds and/or the presence of polyaromatics may have a more pronounced effect on the catalyst. The inhibition followed LHHW behavior for both cuts. As the concentration of the cut was reduced, the amount of inhibition decreased according to LHHW relationships.

The inhibition displayed by both Cut 4 and Cut 8 are temperature dependent. The value of the inhibition constant (K_I) is dependent on temperature.

Cut 4 nitrogen extracts each exhibited as much or more inhibition than the whole of Cut 4 at the same total nitrogen concentration. The nitrogen containing species are obviously important factors in the inhibition of quinoline conversion, and are likely the major contributors to inhibition of the cut. Further study is warranted to validate this conclusion for other fractions (i.e. Cut 8).

The Cut 8 methanol extract displayed inhibition on quinoline conversion, however the results are difficult to quantify since the catalyst had been damaged by methylene chloride contamination.

Cut 2 exhibited inhibition as well as permanent deactivation of the catalyst. The deactivation made quantitative inhibition values hard to determine, but LHHW behavior did not seem to be followed.

6.2 Deactivation

Deactivation was noted for the Cut 4 nitrogen extracts and Cut 2. No deactivation was apparent for Cut 4 as a whole. Cut 8 displayed unexplained deactivation on the catalyst once, however, it was not noticed during other reactions series, leading to the suspicion of the deactivation result. Cut 8 did not consistently exhibit deactivation of the catalyst.

Deactivation was caused by either the methanol or methylene chloride nitrogen extracts of Cut 4. The deactivation was not attributable to one extract or the other.

Cut 2 severely deactivated the catalyst. Two reaction series were carried out with different concentrations of the cut and the deactivation does not appear to be dependent on the concentration of Cut 2. The deactivation caused by Cut 2 is not likely a result of high molecular weight or polyaromatics as both Cut 4 and Cut 8 had more of those species present than Cut 2. Further investigation into the unusual behavior of Cut 2 is required. The hypothesis that larger polyaromatics or higher molecular weight compounds would be more likely to deactivate the catalyst does not appear to be correct, and other factors or chemical compounds are important.

6.3 Quinoline Intermediates

The method of reaction and analysis in this work was easily applied to study quinoline derivative Decahydroquinoline (DHQ). Cut 8 had a significant impact on the conversion of DHQ. Further study is required to determine the detailed interactions of the gas oil cuts with the reactions of DHQ and other quinoline intermediates.

7 Recommendations

Although this study showed that different gas oil fractions affected the conversion of quinoline and some of those effects were quantified to meet the objectives for this study, several areas for further study were made apparent.

The unusual behavior of Cut 2 makes it an obvious candidate for further study. The observed inhibition and deactivation suggests that not only are the high molecular weight species a concern in hydrotreating, but other species may also be of interest. Detailed analysis of nitrogen extracts from Cut 2 may reveal some information about which types of compounds may be responsible for the inhibition and deactivation noted in this study. Also, because Cut 2 was used in such a large amounts, nearly completely replacing the carrier gas oil in the feedstock in order to obtain the required nitrogen concentration, it may be beneficial to study the effects of Cut 2 at lower total nitrogen concentrations or with Cut 2 nitrogen extracts.

Because the Cut 8 nitrogen extracts were contaminated with methylene chloride little conclusive evidence could be obtained. Further study with non-contaminated extracts is warranted in order to quantify the effects of the nitrogen compounds in Cut 8.

Due to the short amount of time available, the effects of the cuts on different quinoline intermediates were not investigated significantly. Further study of the cut affects on the quinoline hydrodentirogenation pathway compounds will suggest how the cuts affect the nitrogen removal from quinoline. This information could prove invaluable in determining which reaction pathways are most critical to increasing the hydrodenitrogenation rate in commercial hydrotreating reactors.

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Appendix A

Raw Data for Quinoline Conversion

This appendix details the raw data (area counts) obtained from the gas chromatograph for each of the reaction series detailed in the results chapter. The calculation from GC area to extent of conversion is detailed below and the extent of quinoline conversion is shown for each reaction. A sample GC analysis plot is shown in Figure A.1.

From the GC integration, the area of quinoline (A_Q) and 2,7-dimethylquinoline (A_{DMQ}) was obtained. Quinoline was the compound of interest and DMQ was the internal standard. The area ratio of quinoline to DMQ was then calculated, by dividing the areas as shown in Equation A.1.

$$AR = \frac{A_Q}{A_{DMQ}} \qquad \text{Equation A.1}$$

Using the calibration equation, the area ratio was converted into a mass ratio of quinoline to DMQ. The calibration method and equations are shown in a separate appendix. This mass ratio is the mass ratio of the quinoline to DMQ in the final diluted sample fed to the GC.

$$MR = Cal_{C1} \times \frac{A_Q}{A_{DMQ}} + Cal_{C2} \qquad \text{Equation A.2}$$

Once the mass ratio, MR, was known, the concentration of DMQ fed to the GC was required, C_{DMQ}. To aid in consistency and repeatability, the same amount

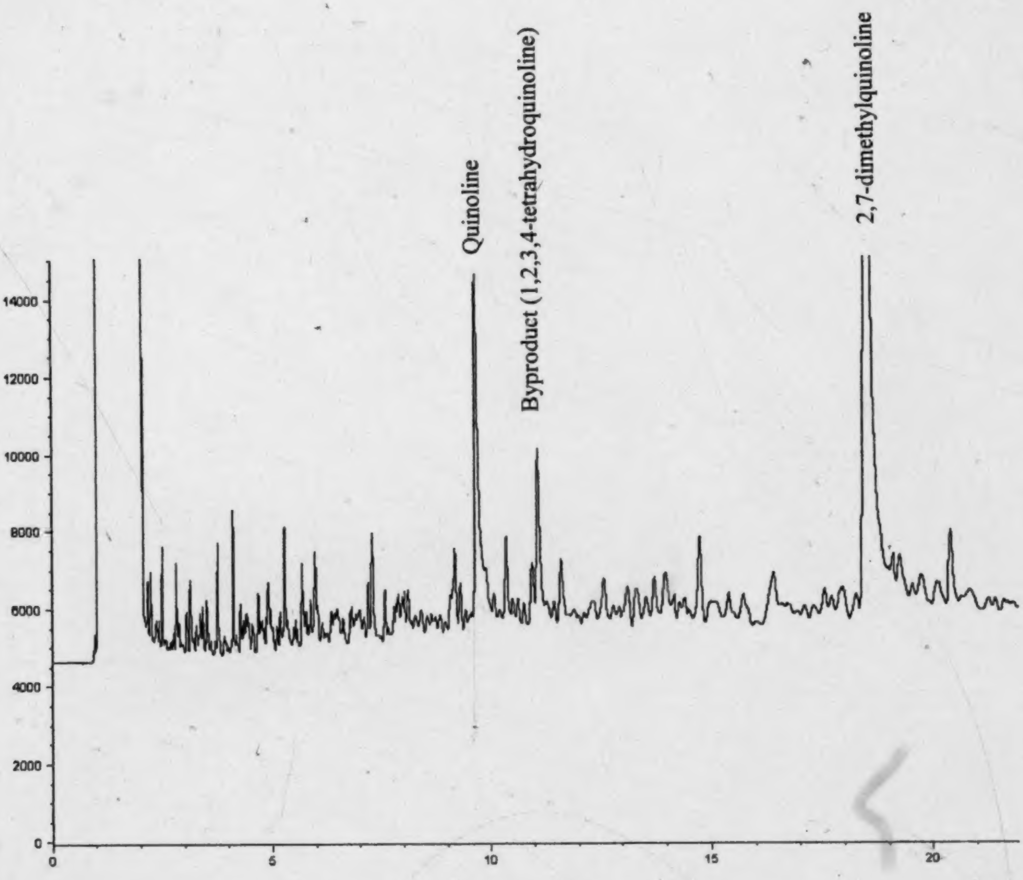

Figure A.1: GC Analysis of Quinoline Reaction with Clean Feed (380°C)

of DMQ was added to every GC run. The internal standard solution was prepared by dissolving 0.0638 g of 2,7-DMQ in a 200 mL volumetric flask then filled with methylene chloride. The resulting stock internal standard solution had a concentration of 3.19×10^{-4} g/mL. An aliquot of 3 mL of this solution was placed in the diluted 10 mL volumetric flask. Therefore the amount of DMQ fed to the GC was always 9.57×10^{-5} g/mL.

$$C_{DMQ} = \frac{3mL \times 3.19x10^{-4}\, g/mL}{10mL} = 9.57x10^{-5}\, g/mL \qquad \text{Equation A.3}$$

From the mass ratio and the concentration of DMQ, the concentration of quinoline (C_{Q2}) in the 2nd diluted 10 mL flask fed to the GC was then determined.

$$C_{Q2} = MR \times C_{DMQ} \qquad \text{Equation A.4}$$

The concentration of quinoline in the 1st diluted 10 mL flask, C_{Q1}, then can be calculated, knowing that 4 mL of the 1st diluted flask was used to make the 2nd 10 mL diluted flask.

$$C_{Q1} = \frac{4mL}{10mL} \times C_{Q2} \qquad \text{Equation A.5}$$

From the concentration, C_{Q1}, the actual mass in the 1st diluted flask could then be determined, M_{Q1}.

$$M_{Q1} = 10mL \times C_{Q1} \qquad \text{Equation A.6}$$

Since all of the quinoline mass came from the oil, the mass fraction of quinoline in the oil can be determined, F_{Qoil}. Dividing the mass of quinoline, M_{Q1}, by the mass of oil used, M_{oil}, gives the wt fraction of quinoline in the oil.

$$F_{Qoil} = \frac{M_{Q1}}{M_{oil}}$$ Equation A.7

The mass fraction of quinoline in the feed oil, F_{QFeed}, was determined from the actual weight of the feed components. Typically, F_{QFeed}, was equal to 0.01 for this study. Some exceptions are the variable quinoline concentration reactions used to develop the reaction kinetics. The extent of conversion was therefore the mass fraction of quinoline in the product oil compared to the feed.

$$Conversion = \left(1 - \frac{F_{Qoil}}{F_{QFeed}}\right) x100\%$$ Equation A.8

The following tables detail the raw data from this work and the GC area counts and corresponding extent of conversions for all of the reactions detailed in the Results section of this work.

Table A.1: Raw Data from Catalyst 2A

Reactions were at 330 °C and 30 minutes reaction time

Cut 4 and Cut 8 at 3000ppm total nitrogen was examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	83186	228991	0.363	0.397	9.570E-05	0.004323	0.010055	57.01
2	Clean Feed	70210	259609	0.270	0.305	9.570E-05	0.003457	0.010055	65.62
3	Clean Feed	82523	241332	0.342	0.376	9.570E-05	0.004327	0.010055	56.96
4	Cut 4, no CS2	73526	233615	0.315	0.409	9.570E-05	0.004893	0.010238	52.21
5	Cut 4, no CS2	69571	240253	0.290	0.384	9.570E-05	0.004478	0.010238	56.26
6	Cut 4, no CS2	115091	244044	0.472	0.567	9.570E-05	0.006745	0.010238	34.12
7	Cut 4, no CS2	100982	227745	0.443	0.538	9.570E-05	0.005963	0.010238	41.76
8	Cut 4, no CS2	106403	230317	0.462	0.557	9.570E-05	0.006469	0.010238	36.81
9	Cut 4, with CS2	110543	234275	0.472	0.567	9.570E-05	0.006309	0.010238	38.38
10	Cut 4, with CS2	111038	224872	0.494	0.589	9.570E-05	0.006743	0.010238	34.14
11	Cut 4, with CS2	104888	219008	0.479	0.574	9.570E-05	0.006448	0.010238	37.02
12	Cut 4, with CS2	85023	230070	0.370	0.464	9.570E-05	0.005364	0.010238	47.61
13	Cut 8	106378	217300	0.490	0.542	9.570E-05	0.006264	0.010186	38.50
14	Cut 8	105288	222958	0.472	0.526	9.570E-05	0.006170	0.010187	39.43
15	Cut 8	106914	225174	0.475	0.528	9.570E-05	0.006228	0.010177	38.80
16	Cut 8	109127	238537	0.457	0.513	9.570E-05	0.006132	0.010200	39.88
17	Cut 8	119002	235529	0.505	0.556	9.570E-05	0.006309	0.010183	38.04
18	Cut 8	116705	238633	0.489	0.542	9.570E-05	0.006026	0.010184	40.82
19	Cut 8	127203	251827	0.505	0.556	9.570E-05	0.006278	0.010193	38.41
20	Cut 8, Forgot CS2	135378	233725	0.579	0.624	9.570E-05	0.007251	0.010180	28.77
21	Cut 8	160408	240667	0.667	0.704	9.570E-05	0.008064	0.010191	20.87
22	Cut 8	154054	232808	0.662	0.700	9.570E-05	0.008014	0.010183	21.30
23	Cut 8	166129	240396	0.691	0.727	9.570E-05	0.008283	0.010190	18.71
24-29	Cut 8, Six reactions not analyzed due to GC malfunction								
30	Cut 8	132514	302001	0.439	0.495	9.570E-05	0.005810	0.010190	42.99
31	Cut 8	172596	300701	0.574	0.620	9.570E-05	0.006799	0.010190	33.28
32	Cut 8	168154	289186	0.581	0.626	9.570E-05	0.007036	0.010190	30.95
33	Cut 8	162457	280742	0.579	0.624	9.570E-05	0.007073	0.010190	30.59

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
35	Clean Feed	80067	271725	0.295	0.329	9.570E-05	0.003821	0.009901	61.40
36	Clean Feed	99678	281521	0.354	0.388	9.570E-05	0.004466	0.009901	54.89
37	Clean Feed	101752	283762	0.359	0.393	9.570E-05	0.004629	0.009901	53.24
38	Clean Feed	113571	276177	0.411	0.445	9.570E-05	0.004865	0.009901	50.87
39	Clean Feed	138107	333891	0.414	0.448	9.570E-05	0.004982	0.009901	49.68
40	Clean Feed	75017	280860	0.267	0.302	9.570E-05	0.003340	0.009901	66.27
41	Clean Feed	93652	342268	0.274	0.308	9.570E-05	0.003428	0.009901	65.38
42	Clean Feed	71577	311570	0.230	0.264	9.570E-05	0.002927	0.009901	70.44
43	Clean Feed	78658	257474	0.305	0.340	9.570E-05	0.003764	0.009901	61.98
44	Clean Feed	37786	247263	0.153	0.188	9.570E-05	0.002003	0.009901	79.77

Table A.2: Raw Data from Catalyst 2D

Reactions were at 330 °C, 30 mL of CS2 and 30 minutes reaction time

Only Cut 4 at 3000ppm total nitrogen was examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	41789	348212	0.12001	0.154823166	0.0000957	0.001646286	0.00999696	83.532
2	Clean Feed	77000	295466	0.260605	0.295067612	0.0000957	0.003460536	0.00999696	65.384
3	Clean Feed	95027	302207	0.314443	0.348771483	0.0000957	0.003565965	0.00999696	64.330
4	Clean Feed	124616	332064	0.375277	0.409453421	0.0000957	0.004577651	0.00999696	54.210
5	Clean Feed	84208	301289	0.279492	0.313907678	0.0000957	0.003593417	0.009996365	64.053
6	Clean Feed	106373	308928	0.344329	0.378582966	0.0000957	0.004354614	0.009996365	56.438
7	Clean Feed	88137	347422	0.253689	0.288168177	0.0000957	0.003379619	0.009996365	66.192
8	Clean Feed	132675	359983	0.368559	0.40275219	0.0000957	0.004301717	0.009996365	56.967
9	Cut 4	102379	298486	0.342994	0.437412598	0.0000957	0.004959761	0.010003368	50.419
10	Cut 4	115558	283796	0.407187	0.501947173	0.0000957	0.005773599	0.010003368	42.283
11	Cut 4	116543	313010	0.37233	0.466904552	0.0000957	0.005613413	0.010003368	43.885
12	Cut 4	116380	297272	0.391493	0.486170014	0.0000957	0.005486612	0.010003368	45.152
13	Cut 4	126997	295285	0.430083	0.524965116	0.0000957	0.005841763	0.010003368	41.602
14	Cut 4	127637	287130	0.444527	0.539486146	0.0000957	0.006296198	0.010003368	37.059
15	Clean Feed	40066	279113	0.143548	0.178301841	0.0000957	0.002111818	0.009996365	78.874
16	Clean Feed	46171	294757	0.156641	0.191362488	0.0000957	0.00207165	0.009988515	79.260
17	Clean Feed	73032	299894	0.243526	0.278030968	0.0000957	0.003065388	0.009988515	69.311
18	Clean Feed	107202	324726	0.330131	0.364419584	0.0000957	0.004337681	0.009988515	56.573
19	Clean Feed	68406	277974	0.246088	0.280586298	0.0000957	0.003274647	0.009988515	67.216
20	Clean Feed	90907	275952	0.32943	0.363721178	0.0000957	0.004124184	0.009988515	58.711
21	Clean Feed	127088	307697	0.41303	0.447111921	0.0000957	0.005218123	0.009988515	47.759
22	Clean Feed	97171	317968	0.3056	0.339950059	0.0000957	0.003948206	0.009988515	60.473
23	Clean Feed	127062	275569	0.46109	0.49505197	0.0000957	0.005508892	0.009988515	44.848
24	Clean Feed	119761	316421	0.378486	0.412654621	0.0000957	0.00476945	0.009988515	52.251

Table A.3: Raw Data from Catalyst 3A

Reactions were at 330 °C, 30 mL of CS2 and 30 minutes reaction time

Cut 4 and Cut 8 at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	118390	354630	0.333841	0.449751	9.57E-05	0.0051485	0.0099994	48.51
2	Clean Feed	155302	302239	0.513838	0.649815	9.57E-05	0.0075470	0.0099994	24.53
3	Clean Feed	125952	337937	0.372709	0.492952	9.57E-05	0.0056430	0.0099994	43.57
4	Clean Feed	59354	324360	0.182988	0.282081	9.57E-05	0.0031985	0.0099994	68.01
5	Clean Feed	71311	311666	0.228806	0.333006	9.57E-05	0.0038304	0.0099994	61.69
6	Clean Feed	101637	298918	0.340016	0.456615	9.57E-05	0.0052270	0.0099994	47.73
7	Clean Feed	170400	310161	0.549392	0.689332	9.57E-05	0.0078162	0.0099994	21.83
8	Clean Feed	184111	378563	0.486342	0.619253	9.57E-05	0.0069232	0.0099994	30.76
9	Clean Feed	114174	338836	0.336959	0.453217	9.57E-05	0.0053679	0.0099961	46.30
10	Clean Feed	97689	354800	0.275335	0.384723	9.57E-05	0.0045794	0.0099961	54.19
11	Clean Feed	106884	318221	0.33588	0.452017	9.57E-05	0.0051254	0.0099961	48.73
12	Clean Feed	108136	329716	0.327967	0.443222	9.57E-05	0.0045317	0.0099961	54.67
13	Clean Feed	56085	310325	0.18073	0.279571	9.57E-05	0.0031551	0.0099961	68.44
14	Clean Feed	90107	286325	0.314702	0.428478	9.57E-05	0.0047024	0.0099961	52.96
15	Cut 8	121365	281300	0.431443	0.558234	9.57E-05	0.0065150	0.0099975	34.83
16	Cut 8	151961	292226	0.520012	0.656677	9.57E-05	0.0075898	0.0100339	24.36
17	Cut 8	150364	308349	0.487642	0.620698	9.57E-05	0.0071740	0.0100166	28.38
18	Cut 8	164836	289103	0.570164	0.712419	9.57E-05	0.0082741	0.0100139	17.37
19	Cut 8	170976	302516	0.56518	0.70688	9.57E-05	0.0081701	0.0100127	18.40
20	Cut 8	151719	297821	0.50943	0.644915	9.57E-05	0.0076384	0.0099945	23.57
21	Clean Feed	105761	334490	0.316186	0.430128	9.57E-05	0.0047643	0.0099981	52.35
22	Clean Feed	113005	321234	0.351784	0.469694	9.57E-05	0.0052758	0.0099981	47.23
23	Clean Feed	120857	350433	0.344879	0.46202	9.57E-05	0.0051896	0.0099981	48.09
24	Clean Feed	84488	292848	0.288505	0.39936	9.57E-05	0.0045283	0.0099993	54.71
25	Clean Feed	138211	287802	0.480229	0.612459	9.57E-05	0.0065125	0.0099993	34.87
26	Clean Feed	58206	276630	0.210411	0.312561	9.57E-05	0.0034303	0.0099993	65.69
27	Clean Feed	92558	265142	0.349088	0.466698	9.57E-05	0.0053425	0.0099993	46.57
28	Clean Feed	97541	314205	0.310437	0.423738	9.57E-05	0.0049696	0.0099993	50.30

Table A.3: Raw Data from Catalyst 3A

Reactions were at 330 °C, 30 mL of CS2 and 30 minutes reaction time

Cut 4 and Cut 8 at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
29	Clean Feed	79707	325830	0.244628	0.350592	9.57E-05	0.0042150	0.0099961	57.83
30	Clean Feed	79755	273974	0.291104	0.40225	9.57E-05	0.0046047	0.0099961	53.94
31	Cut 4	94030	256051	0.367232	0.486864	9.57E-05	0.0057380	0.0100034	42.64
32	Cut 4	130086	271208	0.479654	0.611819	9.57E-05	0.0068083	0.0100034	31.94
33	Cut 4	122869	274883	0.446987	0.57551	9.57E-05	0.0066840	0.0100034	33.18
34	Cut 4	148667	266236	0.558403	0.699348	9.57E-05	0.0076752	0.0100034	23.27
35	Cut 4	173532	296347	0.58557	0.729544	9.57E-05	0.0081945	0.0100034	18.08
36	Cut 4	134694	289090	0.465924	0.596559	9.57E-05	0.0068950	0.0100034	31.07
37	Cut 4	148192	272001	0.544822	0.684252	9.57E-05	0.0071488	0.0100034	28.54
38	Clean Feed	126642	331881	0.381589	0.502822	9.57E-05	0.0052304	0.0099961	47.68
39	Clean Feed	119541	277128	0.431357	0.558138	9.57E-05	0.0063892	0.0099961	36.08
40	Clean Feed	66761	312197	0.213843	0.316375	9.57E-05	0.0036567	0.0099961	63.42
41	Clean Feed	74031	310623	0.238331	0.343593	9.57E-05	0.0038594	0.0099961	61.39
42	Clean Feed	88924	263283	0.337751	0.454097	9.57E-05	0.0051006	0.0099961	48.97
43	Clean Feed	174045	289140	0.60194	0.747738	9.57E-05	0.0082063	0.0099961	17.91
44	Clean Feed	82057	311321	0.263577	0.371654	9.57E-05	0.0041166	0.0099961	58.82
45	Clean Feed	132418	296763	0.446208	0.574645	9.57E-05	0.0063357	0.0099961	36.62
46	Clean Feed	73870	261303	0.282699	0.392907	9.57E-05	0.0045194	0.0099961	54.79
47	Clean Feed	87255	309373	0.282038	0.392173	9.57E-05	0.0045769	0.0099961	54.21

Table A.4: Raw Data from Catalyst 3B

Reactions were at 350 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 4 and Cut 8 at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	111745	280912	0.398	0.521	0.0000957	0.005742366	0.00999934	42.57
2	Clean Feed	93390	320465	0.291	0.403	0.0000957	0.004653253	0.00999934	53.46
3	Clean Feed	120412	298549	0.403	0.527	0.0000957	0.006032536	0.00999934	39.67
4	Clean Feed	63831	288472	0.221	0.325	0.0000957	0.003716199	0.00999673	62.83
5	Clean Feed	70751	271540	0.261	0.368	0.0000957	0.004098348	0.00999673	59.00
6	Clean Feed	73107	264475	0.276	0.386	0.0000957	0.004526189	0.00999705	54.72
7	Clean Feed	80659	308452	0.261	0.369	0.0000957	0.004418242	0.00999874	55.81
8	Clean Feed	116940	312890	0.374	0.494	0.0000957	0.005656142	0.00999874	43.43
9	Clean Feed	90402	290000	0.312	0.425	0.0000957	0.00493803	0.00999874	50.61
10	Clean Feed	70104	256076	0.274	0.383	0.0000957	0.0044479	0.00999874	55.52
11	Clean Feed	55249	263031	0.210	0.312	0.0000957	0.003489884	0.00999874	65.10
12	Clean Feed	107181	262604	0.408	0.532	0.0000957	0.005815639	0.00999874	41.84
13	Clean Feed	91205	258660	0.353	0.471	0.0000957	0.005336156	0.00999874	46.63
14	Clean Feed	161132	298143	0.540	0.679	0.0000957	0.00800716	0.00999874	19.92
15	Clean Feed	98407	301157	0.327	0.442	0.0000957	0.005233701	0.00999874	47.66
16	Cut 4	105530	266966	0.395	0.518	0.0000957	0.00613587	0.0099951	38.61
17	Cut 4	118511	268654	0.441	0.569	0.0000957	0.006352455	0.0099951	36.44
18	Cut 4	85716	256786	0.334	0.450	0.0000957	0.005182702	0.0099951	48.15
19	Cut 4	117528	262208	0.448	0.577	0.0000957	0.006566126	0.0099951	34.31
20	Cut 4	119680	261411	0.458	0.588	0.0000957	0.006993657	0.0099951	30.03
21	Cut 4	142836	278947	0.512	0.648	0.0000957	0.007384171	0.0099951	26.12
22	Cut 4	96733	253967	0.381	0.502	0.0000957	0.005719704	0.0099951	42.77
23	Cut 4	111508	259630	0.429	0.556	0.0000957	0.006521451	0.0099951	34.75
24	Cut 4	147670	263618	0.560	0.701	0.0000957	0.007079658	0.0099951	29.17
25	Cut 4	143540	286607	0.501	0.635	0.0000957	0.007170174	0.0099951	28.26
26	Cut 4	121357	273711	0.443	0.571	0.0000957	0.006449566	0.0099951	35.47
27	Clean Feed	96619	271638	0.356	0.474	0.0000957	0.005426466	0.01000031	45.74
28	Clean Feed	57738	268474	0.215	0.318	0.0000957	0.003672292	0.01000031	63.28
29	Clean Feed	108353	292027	0.371	0.491	0.0000957	0.005703608	0.01000031	42.97
30	Clean Feed	85578	291279	0.294	0.405	0.0000957	0.004706571	0.01000031	52.94
31	Clean Feed	102065	283921	0.359	0.478	0.0000957	0.005527629	0.01000031	44.73

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
32	Clean Feed	76882	285915	0.269	0.378	0.0000957	0.00430158	0.01000031	56.99
33	Clean Feed	72272	256018	0.282	0.392	0.0000957	0.004118206	0.01000031	58.82
34	Clean Feed	183493	308146	0.595	0.741	0.0000957	0.008240789	0.00999808	17.58
35	Clean Feed	88858	274878	0.323	0.438	0.0000957	0.005037987	0.00999808	49.61
36	Clean Feed	90190	289913	0.311	0.424	0.0000957	0.004882396	0.00999808	51.17
37	Clean Feed	63696	299422	0.213	0.315	0.0000957	0.003677894	0.00999808	63.21
38	Clean Feed	108438	281506	0.385	0.507	0.0000957	0.006003079	0.00999808	39.96
39	Cut 8	119573	243723	0.491	0.624	0.0000957	0.007177467	0.00996632	27.98
40	Cut 8	154992	256595	0.604	0.750	0.0000957	0.008011298	0.00996454	19.60
41	Cut 8	122868	255210	0.481	0.614	0.0000957	0.007094321	0.00998037	28.92
42	Cut 8	165106	285951	0.577	0.720	0.0000957	0.007980031	0.01001721	20.34
43	Cut 8	127095	258182	0.492	0.626	0.0000957	0.006775223	0.00999368	32.20
44	Cut 8	145210	258090	0.563	0.704	0.0000957	0.007945462	0.01000707	20.60
45	Cut 8	142038	256231	0.554	0.695	0.0000957	0.007522051	0.00998997	24.70
46	Cut 8	156836	254134	0.617	0.765	0.0000957	0.008837589	0.00999548	11.58
47	Cut 8	136656	268194	0.510	0.645	0.0000957	0.00763988	0.00997106	23.38
48	Clean Feed	108367	242155	0.448	0.576	0.0000957	0.006594749	0.01	34.05
49	Clean Feed	120651	264923	0.455	0.585	0.0000957	0.00669537	0.01	33.05
50	Clean Feed	116939	284660	0.411	0.535	0.0000957	0.006374746	0.01	36.25
51	Clean Feed	91388	251644	0.363	0.482	0.0000957	0.005508378	0.01	44.92
52	Clean Feed	106019	253969	0.417	0.543	0.0000957	0.006245119	0.01	37.55
53	Clean Feed	127375	292381	0.436	0.563	0.0000957	0.006077413	0.01	39.23
54	Clean Feed	117200	288803	0.406	0.530	0.0000957	0.00610216	0.01	38.98
55	Clean Feed	101045	249668	0.405	0.529	0.0000957	0.006294203	0.01	37.06
56	Clean Feed	95950	288315	0.333	0.449	0.0000957	0.005135166	0.01000061	48.65
57	Clean Feed	109696	275721	0.398	0.521	0.0000957	0.005769663	0.01000061	42.31
58	Clean Feed	95570	245180	0.390	0.512	0.0000957	0.005777472	0.01000061	42.23
59	Clean Feed	103815	256116	0.405	0.529	0.0000957	0.005972503	0.01000061	40.28
60	Clean Feed	123359	296553	0.416	0.541	0.0000957	0.005937821	0.01000061	40.63
61	Clean Feed	107819	249331	0.432	0.559	0.0000957	0.005947589	0.01000061	40.53
62	Clean Feed	132380	301098	0.440	0.567	0.0000957	0.005953591	0.01000061	40.47

Table A.5: Raw Data from Catalyst 3C

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 4, Cut 8, and Cut 4 Nitrogen Extracts at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	104666	284386	0.368	0.488	0.0000957	0.005280441	0.01	47.20
2	Clean Feed	65495	266719	0.246	0.352	0.0000957	0.004123851	0.01	58.76
3	Clean Feed	92543	266119	0.348	0.465	0.0000957	0.005325443	0.01	46.75
4	Clean Feed	79496	246378	0.323	0.437	0.0000957	0.004935345	0.01	50.65
5	Clean Feed	47266	244111	0.194	0.294	0.0000957	0.003463863	0.01	65.36
6	Clean Feed	95038	281758	0.337	0.454	0.0000957	0.005119044	0.01	48.81
7	Clean Feed	80182	245699	0.326	0.441	0.0000957	0.005028995	0.01	49.71
8	Clean Feed	82353	264505	0.311	0.425	0.0000957	0.004619157	0.01	53.81
9	Clean Feed	62925	234136	0.269	0.377	0.0000957	0.0043411	0.00999652	56.57
10	Clean Feed	85481	267512	0.320	0.434	0.0000957	0.004761477	0.00999652	52.37
11	Clean Feed	65034	242613	0.268	0.377	0.0000957	0.004077348	0.00999652	59.21
12	Clean Feed	98357	262220	0.375	0.496	0.0000957	0.004920036	0.00999652	50.78
13	Cut 4	85602	221231	0.387	0.509	0.0000957	0.005852008	0.00999567	41.45
14	Cut 4	86552	200937	0.431	0.557	0.0000957	0.006351002	0.00999567	36.46
15	Cut 4	88981	210164	0.423	0.549	0.0000957	0.006538087	0.00999567	34.59
16	Cut 4	105437	222734	0.473	0.605	0.0000957	0.006762077	0.00999567	32.35
17	Cut 4	91653	231358	0.396	0.519	0.0000957	0.00611689	0.00999567	38.80
18	Cut 4	108628	230989	0.470	0.601	0.0000957	0.006917468	0.00999567	30.80
19	Cut 4	109420	232660	0.470	0.601	0.0000957	0.006630893	0.00999567	33.66
20	Cut 4	112210	224481	0.500	0.634	0.0000957	0.006774649	0.0099951	32.22
21	Clean Feed	99547	252153	0.395	0.517	0.0000957	0.005602267	0.00999652	43.96
22	Clean Feed	82686	250083	0.331	0.446	0.0000957	0.004896797	0.00999652	51.01
23	Clean Feed	79138	277349	0.285	0.396	0.0000957	0.004509749	0.00999652	54.89
24	Clean Feed	101252	294002	0.344	0.461	0.0000957	0.004973366	0.01000102	50.27
25	Clean Feed	114866	285956	0.402	0.525	0.0000957	0.005392523	0.01000102	46.08
26	Clean Feed	66646	234867	0.284	0.394	0.0000957	0.004405862	0.01000102	55.95

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 4, Cut 8, and Cut 4 Nitrogen Extracts at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
27	Clean Feed	107953	267826	0.403	0.527	0.0000957	0.005207141	0.01000102	47.93
28	Clean Feed	73002	242854	0.301	0.413	0.0000957	0.004530437	0.01000102	54.70
29	Clean Feed	73345	260872	0.281	0.391	0.0000957	0.004141243	0.01000102	58.59
30	Clean Feed	72353	239762	0.302	0.414	0.0000957	0.004717837	0.01000102	52.83
31	Clean Feed	83268	247321	0.337	0.453	0.0000957	0.005063451	0.01000102	49.37
32	Clean Feed	104231	302708	0.344	0.461	0.0000957	0.004737845	0.01000102	52.63
33	Clean Feed	76386	235533	0.324	0.439	0.0000957	0.005175801	0.00999181	48.20
34	Clean Feed	112703	281343	0.401	0.524	0.0000957	0.006205583	0.00999181	37.89
35	Cut 8	100884	234642	0.430	0.557	0.0000957	0.006281135	0.00999898	37.18
36	Cut 8	122904	255359	0.481	0.614	0.0000957	0.007126953	0.0099588	28.44
37	Cut 8	124684	224917	0.554	0.695	0.0000957	0.007954192	0.01001198	20.55
38	Cut 8	116092	247807	0.468	0.599	0.0000957	0.007029693	0.00999009	29.63
39	Cut 8	128599	229229	0.561	0.702	0.0000957	0.008235847	0.00996435	17.35
40	Cut 8	139549	249041	0.560	0.702	0.0000957	0.007393632	0.00999693	26.04
41	Cut 8	117142	252577	0.464	0.594	0.0000957	0.006801842	0.00999459	31.94
42	Cut 8	109300	240505	0.454	0.584	0.0000957	0.006949168	0.00998638	30.41
43	Clean Feed	118382	258185	0.459	0.588	0.0000957	0.006283786	0.00999839	37.15
44	Clean Feed	96224	284886	0.338	0.454	0.0000957	0.005248595	0.00999839	47.51
45	Clean Feed	100622	267910	0.376	0.496	0.0000957	0.005706856	0.00999839	42.92
46	Clean Feed	146306	279879	0.523	0.660	0.0000957	0.006659801	0.00999839	33.39
47	Clean Feed	95855	274120	0.350	0.467	0.0000957	0.005129155	0.00999839	48.70
48	Clean Feed	107812	266978	0.404	0.528	0.0000957	0.005870364	0.00999839	41.29
49	Clean Feed	82645	265178	0.312	0.425	0.0000957	0.004889622	0.00999839	51.10
50	Clean Feed	76225	254367	0.300	0.412	0.0000957	0.004646929	0.00999839	53.52
51	Clean Feed	90063	271803	0.331	0.447	0.0000957	0.005141422	0.00999839	48.58
52	Clean Feed	82119	231650	0.354	0.473	0.0000957	0.005437286	0.00999832	45.62
53	Clean Feed	82793	241122	0.343	0.460	0.0000957	0.005219703	0.00999832	47.79
54	Clean Feed	77145	242328	0.318	0.433	0.0000957	0.004790898	0.00999832	52.08

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 4, Cut 8, and Cut 4 Nitrogen Extracts at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
55	Clean Feed	79709	231201	0.345	0.462	0.0000957	0.004977779	0.00999832	50.21
56	Clean Feed	90115	237134	0.380	0.501	0.0000957	0.00510137	0.00999832	48.98
57	Clean Feed	150074	254682	0.589	0.575	0.0000957	0.006714655	0.00999904	32.85
58	Clean Feed	79328	222464	0.357	0.386	0.0000957	0.004598853	0.00999904	54.01
59	Clean Feed	91250	217858	0.419	0.437	0.0000957	0.005074563	0.00999904	49.25
60	Clean Feed	107084	218897	0.489	0.494	0.0000957	0.005628861	0.00999904	43.71
61	Clean Feed	90770	220534	0.412	0.431	0.0000957	0.005130618	0.00999904	48.69
62	Cut 4 CH2Cl2 Extract	141185	230160	0.613	0.575	0.0000957	0.006712019	0.01000394	32.91
63	Cut 4 CH2Cl2 Extract	133176	224155	0.594	0.558	0.0000957	0.006454321	0.01000394	35.48
64	Cut 4 CH2Cl2 Extract	121276	220793	0.549	0.520	0.0000957	0.006124441	0.01000394	38.78
65	Cut 4 CH2Cl2 Extract	170286	225494	0.755	0.698	0.0000957	0.007948586	0.01000394	20.55
66	Cut 4 CH2Cl2 Extract	150284	192904	0.779	0.718	0.0000957	0.008466159	0.01000394	15.37
67	Cut 4 CH2Cl2 Extract	171893	218978	0.785	0.723	0.0000957	0.007396887	0.01000394	26.06
68	Cut 4 CH2Cl2 Extract	161079	206633	0.780	0.719	0.0000957	0.008188686	0.01000394	18.15
69	Cut 4 CH2Cl2 Extract	140244	195494	0.717	0.665	0.0000957	0.007799184	0.01000394	22.04
70	Cut 4 CH2Cl2 Extract	146271	202081	0.724	0.671	0.0000957	0.007713261	0.01000394	22.90
71	Cut 4 MeOH Extract	175243	212612	0.824	0.722	0.0000957	0.008223334	0.00998224	17.62
72	Cut 4 MeOH Extract	147714	195771	0.755	0.674	0.0000957	0.008100814	0.00998224	18.85
73	Cut 4 MeOH Extract	147342	205958	0.715	0.647	0.0000957	0.007699555	0.00998224	22.87
74	Clean Feed	97933	187951	0.521	0.498	0.0000957	0.005866644	0.00993017	40.92
75	Clean Feed	115760	227072	0.510	0.490	0.0000957	0.005398894	0.00993017	45.63
76	Clean Feed	117134	190591	0.615	0.565	0.0000957	0.006498954	0.00993017	34.55
77	Clean Feed	158616	184722	0.859	0.740	0.0000957	0.008684242	0.00993017	12.55
78	Clean Feed	108273	220895	0.490	0.476	0.0000957	0.005717512	0.00993017	42.42
79	Clean Feed	128107	227540	0.563	0.528	0.0000957	0.006347144	0.00993017	36.08
80	Clean Feed	90035	176783	0.509	0.489	0.0000957	0.005767017	0.00993017	41.92
81	Clean Feed	153922	219263	0.702	0.628	0.0000957	0.00664656	0.00993017	33.07

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 4, Cut 8, and Cut 4 Nitrogen Extracts at 3000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
82	Clean Feed	91237	171807	0.531	0.505	0.0000957	0.005752886	0.00993017	42.07
83	Clean Feed	120883	181698	0.665	0.601	0.0000957	0.007159214	0.00993017	27.90

Table A.6: Raw Data from Catalyst 4B

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 2 at 3000ppm total nitrogen was examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	87688	185126	0.474	0.498	9.57000E-05	0.005751781	0.00999935	42.48
2	Clean Feed	105046	206002	0.510	0.528	9.57000E-05	0.005305399	0.00999935	46.94
3	Clean Feed	163824	317017	0.517	0.614	9.57000E-05	0.007126931	0.00999935	28.73
4	Clean Feed	166796	314959	0.530	0.629	9.57000E-05	0.007061038	0.01000137	29.40
5	Clean Feed	169839	290356	0.585	0.646	9.57000E-05	0.007507356	0.01000192	24.94
6	Clean Feed	160683	288415	0.557	0.618	9.57000E-05	0.006687053	0.01000192	33.14
7	Clean Feed	99061	248435	0.399	0.454	9.57000E-05	0.005174767	0.00999869	48.25
8	Clean Feed	112339	287461	0.391	0.446	9.57000E-05	0.005308886	0.00999869	46.90
9	Clean Feed	110958	286806	0.387	0.442	9.57000E-05	0.005313563	0.00999869	46.86
10	Clean Feed	96523	285187	0.338	0.392	9.57000E-05	0.004262837	0.00999869	57.37
11	Clean Feed	104295	277724	0.376	0.430	9.57000E-05	0.004925331	0.00999869	50.74
12	Clean Feed	107935	302701	0.357	0.411	9.57000E-05	0.004793011	0.00999869	52.06
13	Cut 2	181210	262385	0.691	0.718	9.57000E-05	0.008585098	0.01000131	14.16
14	Cut 2	176965	257961	0.686	0.713	9.57000E-05	0.008324708	0.01000131	16.76
15	Cut 2	196127	259609	0.755	0.779	9.57000E-05	0.00851149	0.01000131	14.90
16	Cut 2	208693	261561	0.798	0.819	9.57000E-05	0.008559577	0.01000131	14.42
17	Cut 2	161827	234757	0.689	0.716	9.57000E-05	0.008361463	0.01000131	16.40
18	Cut 2	166918	256419	0.651	0.680	9.57000E-05	0.007785143	0.01000131	22.16
19	Cut 2	161103	256979	0.627	0.657	9.57000E-05	0.007633897	0.01000131	23.67
20	Clean Feed	146009	269340	0.542	0.602	9.57000E-05	0.006764007	0.01000096	32.37
21	Clean Feed	130040	269771	0.482	0.540	9.57000E-05	0.006398072	0.01000096	36.03
22	Clean Feed	132434	264549	0.501	0.559	9.57000E-05	0.006691282	0.01000096	33.09
23	Clean Feed	121496	240945	0.504	0.563	9.57000E-05	0.006540086	0.01000096	34.61
24	Clean Feed	148144	255704	0.579	0.641	9.57000E-05	0.007780428	0.01000096	22.20

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 2 at 3000ppm total nitrogen was examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
25	Clean Feed	122070	276349	0.442	0.499	9.57000E-05	0.005876118	0.01000096	41.24
26	Clean Feed	108208	272428	0.397	0.453	9.57000E-05	0.00528241	0.01000096	47.18
27	Clean Feed	138618	239712	0.578	0.640	9.57000E-05	0.00746369	0.00999844	25.35
28	Clean Feed	145145	220000	0.660	0.724	9.57000E-05	0.008699889	0.00999844	12.99
29	Clean Feed	155142	218067	0.711	0.777	9.57000E-05	0.007843602	0.00999844	21.55
30	Clean Feed	176153	279501	0.630	0.693	9.57000E-05	0.008292021	0.00999844	17.07
31	Clean Feed	146242	244621	0.598	0.660	9.57000E-05	0.007699345	0.00999844	22.99

Table A.7: Raw Data from Catalyst 4A

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 2, Cut 4, and Cut 8 at 2000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fractior (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	81086	257832	0.314	0.428	9.5700E-05	0.004902273	0.010000331	50.98
2	Clean Feed	61417	238095	0.258	0.365	9.5700E-05	0.004162966	0.010000331	58.37
3	Clean Feed	102313	250529	0.408	0.533	9.5700E-05	0.004997121	0.010000331	50.03
4	Clean Feed	60628	234306	0.259	0.366	9.5700E-05	0.004193114	0.010000331	58.07
5	Clean Feed	49269	210383	0.234	0.339	9.5700E-05	0.003880516	0.01	61.19
6	Clean Feed	76966	258152	0.298	0.410	9.5700E-05	0.004832997	0.01	51.67
7	Clean Feed	47715	219955	0.217	0.320	9.5700E-05	0.003660953	0.01	63.39
8	Clean Feed	74696	248924	0.300	0.412	9.5700E-05	0.004931198	0.01	50.69
9	Cut 4	53570	184572	0.290	0.401	9.5700E-05	0.004776528	0.009998027	52.23
10	Cut 4	60808	201978	0.301	0.413	9.5700E-05	0.004664453	0.009998027	53.35
11	Cut 4	66120	225144	0.294	0.405	9.5700E-05	0.004822035	0.009998027	51.77
12	Cut 4	72499	203671	0.356	0.474	9.5700E-05	0.005429915	0.009998027	45.69
13	Cut 4	89511	213420	0.419	0.545	9.5700E-05	0.0062975	0.009998027	37.01
14	Cut 4	51336	205085	0.250	0.357	9.5700E-05	0.00416545	0.009998027	58.34
15	Cut 4	86140	224008	0.385	0.506	9.5700E-05	0.005605781	0.009998027	43.93
16	Cut 4	66882	210558	0.318	0.432	9.5700E-05	0.004590897	0.009998027	54.08
17	Clean Feed	37067	193444	0.192	0.292	9.5700E-05	0.003387487	0.01000099	66.13
18	Clean Feed	37020	204739	0.181	0.280	9.5700E-05	0.003041369	0.01000099	69.59
19	Clean Feed	54589	208428	0.262	0.370	9.5700E-05	0.004134319	0.01000099	58.66
20	Clean Feed	52602	198995	0.264	0.373	9.5700E-05	0.004264145	0.01000099	57.36
21	Clean Feed	67697	203561	0.333	0.448	9.5700E-05	0.005083567	0.01000099	49.17
22	Clean Feed	60885	216937	0.281	0.391	9.5700E-05	0.003665109	0.01000099	63.35
23	Clean Feed	46021	218611	0.211	0.313	9.5700E-05	0.003495699	0.01000099	65.05

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 2, Cut 4, and Cut 8 at 2000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fractior (Q/Oil)	Known Feed Fraction	% Conversion
24	Clean Feed	59046	226800	0.260	0.368	9.5700E-05	0.0041537	0.01000099	58.47
25	Clean Feed	45722	203497	0.225	0.328	9.5700E-05	0.003814321	0.01000099	61.86
26	Clean Feed	31593	204543	0.154	0.250	9.5700E-05	0.002965379	0.009998658	70.34
27	Clean Feed	55183	215142	0.256	0.364	9.5700E-05	0.004184381	0.009998658	58.15
28	Clean Feed	46353	218738	0.212	0.314	9.5700E-05	0.003703403	0.009998658	62.96
29	Clean Feed	68665	255481	0.269	0.377	9.5700E-05	0.004362245	0.009998658	56.37
30	Clean Feed	54740	224064	0.244	0.350	9.5700E-05	0.00404799	0.009998658	59.51
31	Clean Feed	63636	211789	0.300	0.413	9.5700E-05	0.004723854	0.009998658	52.76
32	Cut 8	76972	219186	0.351	0.469	9.5700E-05	0.005527667	0.009996002	44.70
33	Cut 8	74198	207302	0.358	0.477	9.5700E-05	0.005671974	0.009995509	43.25
34	Cut 8	75629	210064	0.360	0.479	9.5700E-05	0.005588621	0.010008946	44.16
35	Cut 8	115176	219407	0.525	0.662	9.5700E-05	0.007168369	0.010003369	28.34
36	Cut 8	87784	221956	0.396	0.518	9.5700E-05	0.006159955	0.009999993	38.40
37	Cut 8	91601	223453	0.410	0.534	9.5700E-05	0.006266557	0.010011129	37.40
38	Cut 8	94754	202058	0.469	0.600	9.5700E-05	0.006644905	0.010005026	33.58
39	Cut 8	73507	204682	0.359	0.478	9.5700E-05	0.005470204	0.009991514	45.25
40	Cut 8	74717	209093	0.357	0.476	9.5700E-05	0.005580954	0.009995402	44.16
41	Cut 8	95702	247886	0.386	0.508	9.5700E-05	0.005813037	0.01000137	41.88
42	Cut 8	72870	195994	0.372	0.492	9.5700E-05	0.005685811	0.009986362	43.06
43	Cut 8	81179	214009	0.379	0.500	9.5700E-05	0.00575472	0.009998412	42.44
44	Clean Feed	51628	189288	0.273	0.403	9.5700E-05	0.004565513	0.010000676	54.35
45	Clean Feed	60351	218241	0.277	0.407	9.5700E-05	0.004588987	0.010000676	54.11
46	Clean Feed	62229	201434	0.309	0.441	9.5700E-05	0.004974198	0.010000676	50.26
47	Clean Feed	66858	208313	0.321	0.453	9.5700E-05	0.005165855	0.010000676	48.34
48	Clean Feed	60080	215930	0.278	0.408	9.5700E-05	0.004743506	0.010000676	52.57

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 2, Cut 4, and Cut 8 at 2000ppm total nitrogen were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fractior (Q/Oil)	Known Feed Fraction	% Conversion
49	Clean Feed	74313	237683	0.313	0.445	9.5700E-05	0.004686883	0.010000676	53.13
50	Cut 2	198301	335778	0.591	0.707	9.5700E-05	0.008058914	0.01	19.41
51	Cut 2	167974	324675	0.517	0.607	9.5700E-05	0.007045177	0.01	29.55
52	Cut 2	206939	336480	0.615	0.741	9.5700E-05	0.008690416	0.01	13.10
53	Cut 2	182248	302792	0.602	0.723	9.5700E-05	0.008396338	0.01	16.04
54	Cut 2	189352	329813	0.574	0.685	9.5700E-05	0.007914001	0.01	20.86
55	Cut 2	210445	320732	0.656	0.798	9.5700E-05	0.008875673	0.01	11.24
56	Clean Feed	150241	310049	0.485	0.538	9.5700E-05	0.00601116	0.01	39.89
57	Clean Feed	129474	322033	0.402	0.436	9.5700E-05	0.005211437	0.01	47.89
58	Clean Feed	146810	332111	0.442	0.485	9.5700E-05	0.005606802	0.01	43.93
59	Clean Feed	154298	342633	0.450	0.495	9.5700E-05	0.005837925	0.01	41.62
60	Clean Feed	140194	293951	0.477	0.528	9.5700E-05	0.006256349	0.01	37.44
61	Clean Feed	162549	362926	0.448	0.492	9.5700E-05	0.005582297	0.01	44.18
62	Clean Feed	111613	284245	0.393	0.424	9.5700E-05	0.005098087	0.01	49.02

Table A.8: Raw Data from Catalyst 3D

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

500ppm, 1000ppm, 1500ppm, 2000ppm, and 3000ppm total nitrogen contents due to Quinoline were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	1000 ppm	56114	261911	0.214	0.317	9.57000E-05	0.003609553	0.00999832	63.90
2	1000 ppm	85943	262119	0.328	0.443	9.57000E-05	0.004775549	0.00999832	52.24
3	1000 ppm	101175	295303	0.343	0.460	9.57000E-05	0.005235044	0.00999832	47.64
4	1000 ppm	104867	301872	0.347	0.465	9.57000E-05	0.005172355	0.00999832	48.27
5	1000 ppm	71720	250000	0.287	0.398	9.57000E-05	0.004444625	0.01000033	55.56
6	1000 ppm	98713	279256	0.353	0.472	9.57000E-05	0.004624053	0.01000033	53.76
7	1000 ppm	85878	252748	0.340	0.456	9.57000E-05	0.005101939	0.01000033	48.98
8	1000 ppm	112915	287154	0.393	0.516	9.57000E-05	0.005686332	0.01000033	43.14
9	3000 ppm	379466	258704	1.467	1.655	9.57000E-05	0.018671693	0.02740662	31.87
10	3000 ppm	328300	238789	1.375	1.584	9.57000E-05	0.016192731	0.02740662	40.92
11	3000 ppm	306647	226856	1.352	1.566	9.57000E-05	0.018275661	0.02740662	33.32
12	3000 ppm	289686	223906	1.294	1.521	9.57000E-05	0.018018905	0.02740662	34.25
13	3000 ppm	362663	248796	1.458	1.647	9.57000E-05	0.016916732	0.02740662	38.28
14	3000 ppm	351166	245518	1.430	1.626	9.57000E-05	0.01888936	0.02740662	31.08
15	3000 ppm	456310	219090	2.083	2.129	9.57000E-05	0.023908941	0.02740662	12.76
16	3000 ppm	367587	226887	1.620	1.773	9.57000E-05	0.019016812	0.02740662	30.61
17	500 ppm	63626	306252	0.208	0.252	9.57000E-05	0.002929424	0.00502089	41.66
18	500 ppm	54773	291091	0.188	0.229	9.57000E-05	0.002650419	0.00502089	47.21
19	500 ppm	64549	332138	0.194	0.237	9.57000E-05	0.002747224	0.00502089	45.28
20	500 ppm	78306	342362	0.229	0.277	9.57000E-05	0.00316808	0.00502089	36.90
21	500 ppm	30299	180122	0.168	0.244	9.57000E-05	0.002888834	0.00502089	42.46
22	500 ppm	50823	237753	0.214	0.282	9.57000E-05	0.003370367	0.00502089	32.87
23	500 ppm	52361	243253	0.215	0.283	9.57000E-05	0.003239395	0.00502089	35.48

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

500ppm, 1000ppm, 1500ppm, 2000ppm, and 3000ppm total nitrogen contents due to Quinoline were examined

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
24	500 ppm	0	193473	0.000	0.104	9.57000E-05	0.001153829	0.00502089	77.02
25	500 ppm	31058	237084	0.131	0.213	9.57000E-05	0.002473708	0.00502089	50.73
26	500 ppm	0	188040	0.000	0.104	9.57000E-05	0.001192474	0.00502089	76.25
27	2000 ppm	250959	246369	1.019	0.950	9.57000E-05	0.010984111	0.01979638	44.51
28	2000 ppm	344562	229817	1.499	1.350	9.57000E-05	0.015524027	0.01979638	21.58
29	2000 ppm	240952	225869	1.067	0.990	9.57000E-05	0.011123949	0.01979638	43.81
30	2000 ppm	271680	223656	1.215	1.113	9.57000E-05	0.012929297	0.01979638	34.69
31	2000 ppm	226277	224804	1.007	0.940	9.57000E-05	0.011305055	0.01979638	42.89
32	2000 ppm	299668	212763	1.408	1.274	9.57000E-05	0.014798438	0.01979638	25.25
33	2000 ppm	248678	203134	1.224	1.121	9.57000E-05	0.013344699	0.01979638	32.59
34	2000 ppm	197824	177970	1.112	1.028	9.57000E-05	0.011706668	0.01979638	40.86
35	2000 ppm	206972	175342	1.180	1.085	9.57000E-05	0.012976007	0.01937173	33.02
36	2000 ppm	204574	221093	0.925	0.873	9.57000E-05	0.010186294	0.01937173	47.42
37	1500 ppm	188657	325117	0.580	0.642	9.57000E-05	0.007487846	0.0149982	50.08
38	1500 ppm	194594	340001	0.572	0.633	9.57000E-05	0.007539298	0.0149982	49.73
39	1500 ppm	202217	328944	0.615	0.677	9.57000E-05	0.007751858	0.0149982	48.31
40	1500 ppm	150981	283004	0.533	0.593	9.57000E-05	0.006857406	0.0149982	54.28
41	1500 ppm	188000	310761	0.605	0.667	9.57000E-05	0.007900928	0.0149982	47.32
42	1500 ppm	240491	338724	0.710	0.775	9.57000E-05	0.008963047	0.0149982	40.24
43	1500 ppm	190663	331223	0.576	0.637	9.57000E-05	0.007395863	0.0149982	50.69

Table A.9: Raw Data from Catalyst 4D

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 8 and Cut 8 Nitrogen Extracts at 3000ppm total nitrogen were examined

New Reactor denotes reactor not previously exposed to Cut 8 CH2Cl2 extract

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% reacted
1	Clean Feed	98922	308470	0.321	0.335	9.57E-05	0.003948768	0.0099991	60.51
2	Clean Feed	1E+05	283446	0.396	0.428	9.57E-05	0.005024329	0.0099991	49.75
3	Clean Feed	1E+05	302653	0.478	0.529	9.57E-05	0.005891231	0.0099991	41.08
4	Clean Feed	1E+05	298183	0.345	0.365	9.57E-05	0.004026496	0.0099991	59.73
5	Clean Feed	97490	298848	0.326	0.342	9.57E-05	0.003970719	0.0099991	60.29
6	Clean Feed	1E+05	281963	0.480	0.533	9.57E-05	0.005926827	0.0099991	40.73
7	Clean Feed	1E+05	306091	0.337	0.356	9.57E-05	0.003782015	0.0099991	62.18
8	Clean Feed	1E+05	306923	0.330	0.347	9.57E-05	0.004106543	0.0099991	58.93
9	Cut 8	2E+05	286041	0.640	0.730	9.57E-05	0.008162941	0.0099809	18.21
10	Cut 8	2E+05	277097	0.556	0.626	9.57E-05	0.007168792	0.0099765	28.14
11	Cut 8	2E+05	272110	0.576	0.650	9.57E-05	0.007703077	0.0100043	23.00
12	Cut 8	2E+05	280775	0.569	0.642	9.57E-05	0.007487582	0.0100267	25.32
13	Cut 8	2E+05	263748	0.600	0.681	9.57E-05	0.007983167	0.0100031	20.19
14	Cut 8	2E+05	267504	0.576	0.651	9.57E-05	0.007174671	0.0099815	28.12
15	Cut 8	2E+05	291340	0.567	0.640	9.57E-05	0.007735154	0.0100032	22.67
16	Clean Feed	1E+05	258990	0.513	0.572	9.57E-05	0.006648615	0.0100016	33.52
17	Clean Feed	1E+05	291594	0.389	0.420	9.57E-05	0.004785312	0.0100016	52.15
18	Clean Feed	1E+05	281095	0.401	0.434	9.57E-05	0.004925148	0.0100016	50.76
19	Clean Feed	1E+05	296407	0.361	0.384	9.57E-05	0.004378788	0.0100016	56.22
20	Clean Feed	1E+05	259097	0.416	0.453	9.57E-05	0.005185618	0.0100016	48.15

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 8 and Cut 8 Nitrogen Extracts at 3000ppm total nitrogen were examined

New Reactor denotes reactor not previously exposed to Cut 8 CH2Cl2 extract

Reaction #	Feed Type	GC Q area	GC DMQ are	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	roduct Fractio (Q/Oil)	Known Feed Fraction	% reacted
21	Clean Feed	95460	289693	0.330	0.346	9.57E-05	0.003979497	0.0100016	60.21
22	Clean Feed	83910	284726	0.295	0.303	9.57E-05	0.003660323	0.0100016	63.40
23	Clean Feed	95719	308262	0.311	0.322	9.57E-05	0.003745164	0.0100016	62.55
24	Cut 8 CH2Cl2 Extract	86444	275520	0.314	0.326	9.57E-05	0.003632922	0.0100033	63.68
25	Cut 8 CH2Cl2 Extract	32044	270859	0.118	0.085	9.57E-05	0.000980385	0.0099847	90.18
26	Cut 8 CH2Cl2 Extract	12164	276216	0.044	-0.007	9.57E-05	-8.33268E-05	0.0100095	100.00
27	Cut 8 CH2Cl2 Extract	12747	276454	0.046	-0.004	9.57E-05	-5.05842E-05	0.0100024	100.00
28	Cut 8 CH2Cl2 Extract	15896	248795	0.064	0.018	9.57E-05	0.000200866	0.0099812	97.99
29	Cut 8 CH2Cl2 Extract	0	262714	0.000	-0.061	9.57E-05	-0.000735084	0.0099883	100.00
30	Cut 8 CH2Cl2 Extract	0	259705	0.000	-0.061	9.57E-05	-0.000735084	0.0100175	100.00
31	Cut 8 CH2Cl2 Extract	0	251605	0.000	-0.061	9.57E-05	-0.000668259	0.0099834	100.00
32	Clean Feed	33964	271609	0.125	0.226	9.57E-05	0.002546466	0.0099923	74.52
33	Clean Feed	60804	267358	0.227	0.338	9.57E-05	0.004019673	0.0099923	59.77
34	Clean Feed	43379	261933	0.166	0.270	9.57E-05	0.003121146	0.0099923	68.76
35	Clean Feed	58878	278190	0.212	0.320	9.57E-05	0.00385243	0.0099923	61.45
36	Clean Feed	91044	266390	0.342	0.463	9.57E-05	0.005428404	0.0099923	45.67
37	Clean Feed, New Rxtr	1E+05	273331	0.511	0.649	9.57E-05	0.007496586	0.0099923	24.98
38	Clean Feed, New Rxtr	1E+05	283780	0.495	0.631	9.57E-05	0.007543198	0.0099923	24.51
39	Clean Feed	81680	276748	0.295	0.412	9.57E-05	0.004806284	0.0099923	51.90
40	Clean Feed, New Rxtr	1E+05	276909	0.458	0.590	9.57E-05	0.006883551	0.0099683	30.95
41	Clean Feed	65143	286451	0.227	0.338	9.57E-05	0.004039624	0.0099683	59.48
42	Clean Feed, New Rxtr	1E+05	282548	0.497	0.633	9.57E-05	0.007247898	0.0099683	27.29

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 8 and Cut 8 Nitrogen Extracts at 3000ppm total nitrogen were examined

New Reactor denotes reactor not previously exposed to Cut 8 CH2Cl2 extract

Reaction #	Feed Type	GC Q area	GC DMQ are	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fractior (Q/Oil)	Known Feed Fraction	% reacted
43	Clean Feed	56070	252592	0.222	0.343	9.57E-05	0.004062247	0.0099683	59.25
44	Clean Feed, New Rxtr	91971	257316	0.357	0.500	9.57E-05	0.006035723	0.0099683	39.45
45	Clean Feed	74509	258490	0.288	0.420	9.57E-05	0.004994042	0.0099683	49.90
46	Cut 8 CH2Cl2 Extract	40994	237486	0.173	0.286	9.57E-05	0.003288899	0.0100138	67.16
47	Cut 8 CH2Cl2 Extract	21154	252962	0.084	0.183	9.57E-05	0.002116115	0.0100133	78.87
48	Cut 8 CH2Cl2 Extract	19970	263598	0.076	0.174	9.57E-05	0.002011048	0.0099908	79.87
49	Cut 8 CH2Cl2 Extract	0	260158	0.000	0.086	9.57E-05	0.001034086	0.0100112	100.00
50	Cut 8 CH2Cl2 Extract	0	264445	0.000	0.086	9.57E-05	0.001028942	0.010018	100.00
51	Cut 8 CH2Cl2 Extract	0	275546	0.000	0.086	9.57E-05	0.001044532	0.0100072	100.00
52	Clean Feed	18863	237309	0.079	0.178	9.57E-05	0.002091147	0.0099683	79.02
53	Clean Feed	0	249042	0.000	0.086	9.57E-05	0.001008865	0.0099683	100.00
54	Clean Feed	39354	258444	0.152	0.262	9.57E-05	0.003154985	0.0099683	68.35
55	Clean Feed	32428	271074	0.120	0.225	9.57E-05	0.002572157	0.0099683	74.20
56	Clean Feed	33576	252764	0.133	0.240	9.57E-05	0.002746884	0.0099683	72.44
57	Clean Feed	24881	264094	0.094	0.195	9.57E-05	0.002313413	0.0099683	76.79
58	Clean Feed	29707	248150	0.120	0.235	9.57E-05	0.002811092	0.0099975	71.88
59	Clean Feed	29156	248724	0.117	0.232	9.57E-05	0.002761388	0.0099975	72.38
60	Cut 8 MeOH Extract	72544	254785	0.285	0.434	9.57E-05	0.005061951	0.0099973	49.37
61	Cut 8 MeOH Extract	1E+05	265160	0.521	0.718	9.57E-05	0.008295657	0.0099985	17.03
62	Cut 8 MeOH Extract	73321	245632	0.298	0.450	9.57E-05	0.005333598	0.0099938	46.63
63	Cut 8 MeOH Extract	72669	248255	0.293	0.443	9.57E-05	0.005384422	0.0099926	46.12

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Cut 8 and Cut 8 Nitrogen Extracts at 3000ppm total nitrogen were examined

New Reactor denotes reactor not previously exposed to Cut 8 CH2Cl2 extract

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% reacted
64	Clean Feed, New Rxtr	84609	234585	0.361	0.525	9.57E-05	0.006129492	0.0099975	38.69
65	Clean Feed, New Rxtr	96299	247404	0.389	0.560	9.57E-05	0.006595314	0.0099975	34.03
66	Clean Feed	61303	253915	0.241	0.382	9.57E-05	0.004389161	0.0099975	56.10
67	Clean Feed, New Rxtr	1E+05	243477	0.490	0.681	9.57E-05	0.007984403	0.0099975	20.14
68	Clean Feed, New Rxtr	1E+05	249603	0.429	0.608	9.57E-05	0.007231724	0.0099975	27.66
69	Clean Feed	54108	258172	0.210	0.343	9.57E-05	0.003698964	0.0099975	63.00
70	Clean Feed	79923	269664	0.296	0.448	9.57E-05	0.005251371	0.0099975	47.47
71	Clean Feed	57017	299017	0.191	0.320	9.57E-05	0.003721897	0.0100008	62.78
72	Clean Feed	45526	279180	0.163	0.287	9.57E-05	0.003335679	0.0100008	66.65
73	Clean Feed	40600	259800	0.156	0.279	9.57E-05	0.003371546	0.0100008	66.29
N/A	Clean Feed, No Catalys	87424	259800	0.337	0.496	9.57E-05	0.005818135	0.0100008	41.82
N/A	Clean Feed, No Catalys	48320	251173	0.192	0.323	9.57E-05	0.003857987	0.0100008	61.42

Table A.10: Raw Data from Catalyst 4C

Reactions were at 380 °C, 30 mL of CS2 and 20 minutes reaction time

Catalyst never stablized on Clean Feed

Reaction #	Feed Type	GC Q area	GC DMQ area	area ratio Q/DMQ	mass ratio Q/DMQ	DMQ amt (g/ml)	Product Fraction (Q/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed	71859	167548	0.429	0.460	9.57000E-05	0.005147754	0.01000137	48.53
2	Clean Feed	71741	204631	0.351	0.395	9.57000E-05	0.004462282	0.01000137	55.38
3	Clean Feed	114016	192438	0.592	0.596	9.57000E-05	0.006892554	0.01000137	31.08
4	Clean Feed	58569	167024	0.351	0.395	9.57000E-05	0.004730764	0.01000137	52.70
5	Clean Feed	150231	225676	0.666	0.657	9.57000E-05	0.006747912	0.01000137	32.53
6	Clean Feed	77725	201398	0.386	0.425	9.57000E-05	0.005006113	0.01000137	49.95
7	Clean Feed	151387	330678	0.458	0.545	9.57000E-05	0.006388064	0.01000137	36.13
8	Clean Feed	109007	329369	0.331	0.396	9.57000E-05	0.004472667	0.01000137	55.28
9	Clean Feed	106497	214392	0.497	0.517	9.57000E-05	0.006091012	0.00999647	39.07
10	Clean Feed	118307	225431	0.525	0.540	9.57000E-05	0.005927758	0.00999647	40.70
11	Clean Feed	86613	244836	0.354	0.398	9.57000E-05	0.004348439	0.00999647	56.50
12	Clean Feed	91346	232097	0.394	0.431	9.57000E-05	0.005056013	0.00999647	49.42
13	Clean Feed	83463	239810	0.348	0.393	9.57000E-05	0.00463516	0.00999647	53.63
14	Clean Feed	69513	203189	0.342	0.388	9.57000E-05	0.004577122	0.00999647	54.21
15	Clean Feed	97399	159277	0.612	0.612	9.57000E-05	0.007041204	0.00999647	29.56
16	Clean Feed	156312	230408	0.678	0.668	9.57000E-05	0.007361959	0.00999647	26.35
17	Clean Feed	93136	164747	0.565	0.574	9.57000E-05	0.006762516	0.00999647	32.35
18	Clean Feed	81793	201868	0.405	0.441	9.57000E-05	0.005299024	0.01000192	47.02
19	Clean Feed	91712	168235	0.545	0.557	9.57000E-05	0.005769149	0.01000192	42.32
20	Clean Feed	141540	305330	0.464	0.521	9.57000E-05	0.006265261	0.01000192	37.36
21	Clean Feed	155953	299930	0.520	0.579	9.57000E-05	0.006663803	0.01000192	33.37
22	Clean Feed	131435	290487	0.452	0.510	9.57000E-05	0.006096878	0.01000192	39.04
23	Clean Feed	157752	303029	0.521	0.580	9.57000E-05	0.006085966	0.01000192	39.15
24	Clean Feed	119415	307832	0.388	0.443	9.57000E-05	0.004840122	0.01000192	51.61
25	Clean Feed	124932	251602	0.497	0.555	9.57000E-05	0.006674562	0.01000192	33.27

Appendix B

Raw Data for Decahydroquinoline Conversion

This appendix details the raw data (area counts) obtained from the gas chromatograph for each of the decahydroquinoline reactions detailed in the results chapter. The calculation from GC area to extent of conversion is detailed below and the extent of conversion is shown for each reaction.

From the GC integration, the area of DHQ (A_{DHQ}) and 2,7-dimethylquinoline (A_{DMQ}) was obtained. DHQ was the compound of interest and DMQ was the internal standard. The area ratio of DHQ to DMQ was then calculated, by dividing the areas as shown in Equation B.1.

$$AR = \frac{A_{DHQ}}{A_{DMQ}} \qquad \text{Equation B.1}$$

Using the calibration equation, the area ratio was converted into a mass ratio of DHQ to DMQ. The calibration method and equations are shown in a separate appendix. This mass ratio is the mass ratio of the DHQ to DMQ in the final diluted sample fed to the GC.

$$MR = Cal_{C1} \times \frac{A_{DHQ}}{A_{DMQ}} + Cal_{C2} \qquad \text{Equation B.2}$$

Once the mass ratio, MR, was known, the concentration of DMQ fed to the GC was required, C_{DMQ}. To aid in consistency and repeatability, the same amount of DMQ was added to every GC run. The internal standard solution was prepared by dissolving 0.0638 g of 2,7-DMQ in a 200 mL volumetric flask then filled with methylene chloride. The resulting stock internal standard solution had a concentration of 3.19×10^{-4} g/mL. An aliquot of 3 mL of this solution was placed in the diluted 10 mL volumetric flask. Therefore the amount of DMQ fed to the GC was always 9.57×10^{-5} g/mL.

$$C_{DMQ} = \frac{3mL \times 3.19x10^{-4}\,g/mL}{10mL} = 9.57x10^{-5}\,g/mL \qquad \text{Equation B.3}$$

From the mass ratio and the concentration of DMQ, the concentration of DHQ (C_{DHQ2}) in the 2nd diluted 10 mL flask fed to the GC was then determined.

$$C_{DHQ2} = MR \times C_{DMQ} \qquad \text{Equation B.4}$$

The concentration of DHQ in the 1st diluted 10 mL flask, C_{DHQ1}, then can be calculated, knowing that 4 mL of the 1st diluted flask was used to make the 2nd 10 mL diluted flask.

$$C_{DHQ1} = \frac{4mL}{10mL} \times C_{DHQ2} \qquad \text{Equation B.5}$$

From the concentration, C_{DHQ1}, the actual mass in the 1st diluted flask could then be determined, M_{DHQ1}.

$$M_{DHQ1} = 10mL \times C_{DHQ1} \qquad \text{Equation B.6}$$

Since all of the DHQ mass came from the oil, the mass fraction of DHQ in the oil can be determined, F_{DHQoil}. Dividing the mass of DHQ, M_{DHQ1}, by the mass of oil used, M_{oil}, gives the wt fraction of DHQ in the oil.

$$F_{DHQoil} = \frac{M_{DHQ1}}{M_{oil}} \qquad \text{Equation B.7}$$

The mass fraction of DHQ in the feed oil, $F_{DHQFeed}$, was determined from the actual weight of the feed components. The extent of conversion was therefore the mass fraction of DHQ in the product oil compared to the feed.

$$Conversion = \left(1 - \frac{F_{DHQoil}}{F_{DHQFeed}}\right) x100\% \qquad \text{Equation B.8}$$

The following table, Table B1 shows the raw data from this DHQ work and the GC area counts and corresponding extent of conversion for all of the reactions detailed in the Results section of this work. Also shown in the table are the area counts for the 5,6,7,8-tetrahydroquinoline (THQ) compound found during the reactions of DHQ with Cut 8.

Since no GC calibration equation was available for 5,6,7,8-THQ, the equation was approximated as the same for DHQ. By approximating the equation as the same the mass ratio of THQ to DMQ was determined as shown above. Since it takes one molecule of DHQ to make one molecule of THQ, by approximating the molecular weight of THQ and DHQ as the same, the Conversion value obtained is the approximate % of DHQ that was converted into something other than THQ (i.e. underwent Hydrodenitrogenation or ring breaking).

Figure B.1 shows unreacted DHQ feed, and the cis and trans-DHQ peaks can be seen clearly separated. Figures B.2 and B.3 show typical GC curves for the clean feed and Cut 8 reactions with DHQ. Note how the Cut 8 reactions have little to no DHQ remaining but large concentrations of 5,6,7,8-THQ, unlike the clean feed reactions that have little DHQ and very little to no 5,6,7,8-THQ.

Table B.1: Raw Data for DHQ Reactions

Reactions were at 380 °C, 30 μL of CS2 and 20 minutes reaction time

Reactions examined DHQ reactions in clean feed and with Cut 8

Reaction #	Feed Type	GC DHQ area	GC THQ area	GC DMQ area	area ratio DHQ/DMQ	mass ratio DHQ/DMQ	DMQ amt (g/ml)	Product Fraction (DHQ/Oil)	Known Feed Fraction	% Conversion
1	Clean Feed - DHQ	29491	0	358280	0.0823	0.1267	9.57E-05	0.001546323	0.01	84.54
2	Clean Feed - DHQ	23043	0	273852	0.0841	0.1295	9.57E-05	0.001511051	0.009970366	84.84
3	Clean Feed - DHQ	29201	0	279044	0.1046	0.1608	9.57E-05	0.001748274	0.009970366	82.47
4	Clean Feed - DHQ	27599	0	299298	0.0922	0.1418	9.57E-05	0.001521181	0.009970366	84.74
5	Clean Feed - DHQ	28093	0	301966	0.0930	0.1430	9.57E-05	0.001621903	0.009970366	83.73
6	Clean Feed - DHQ	25274	0	301297	0.0839	0.1291	9.57E-05	0.001528793	0.009970366	84.67
7	Cut 8 - DHQ	0	60414	275617	0.2192	0.3356	9.57E-05	0.003974447	0.010025501	60.36
8	Cut 8 - DHQ	0	59724	275845	0.2165	0.3315	9.57E-05	0.003887472	0.010042751	61.29
9	Cut 8 - DHQ	0	61489	280559	0.2192	0.3355	9.57E-05	0.003934955	0.009998974	60.65
10	Cut 8 - DHQ	0	63540	288142	0.2205	0.3376	9.57E-05	0.003901742	0.009980837	60.91
11	Cut 8 - DHQ	0	65324	292045	0.2237	0.3424	9.57E-05	0.003957505	0.009983428	60.36

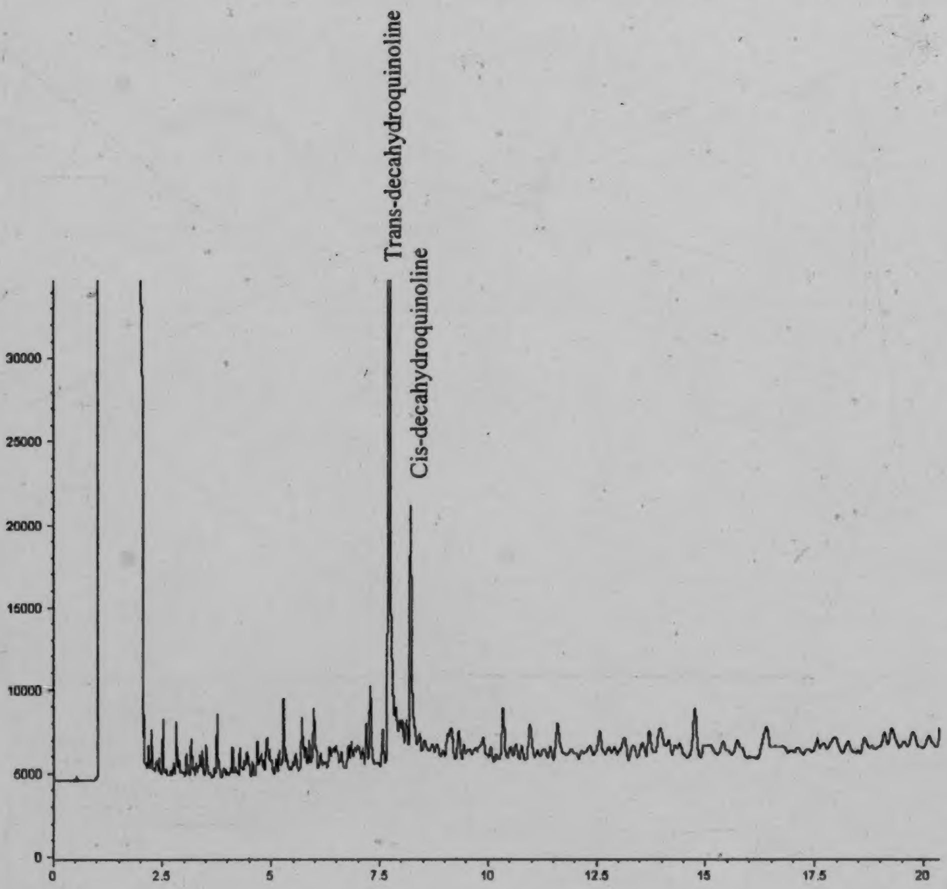

Figure B.1: GC Analysis of Unreacted Decahydroquinoline in Carrier Gas Oil

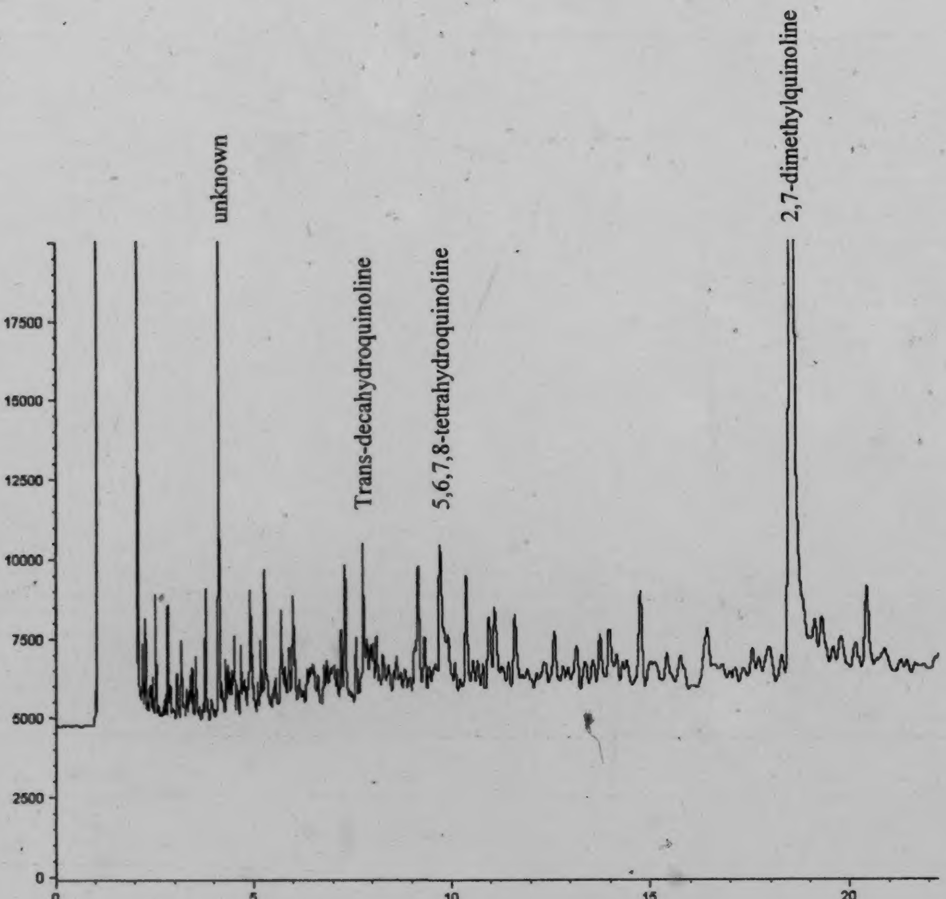

Figure B.2: GC Analysis of Decahydroquinoline Reaction with Clean Feed

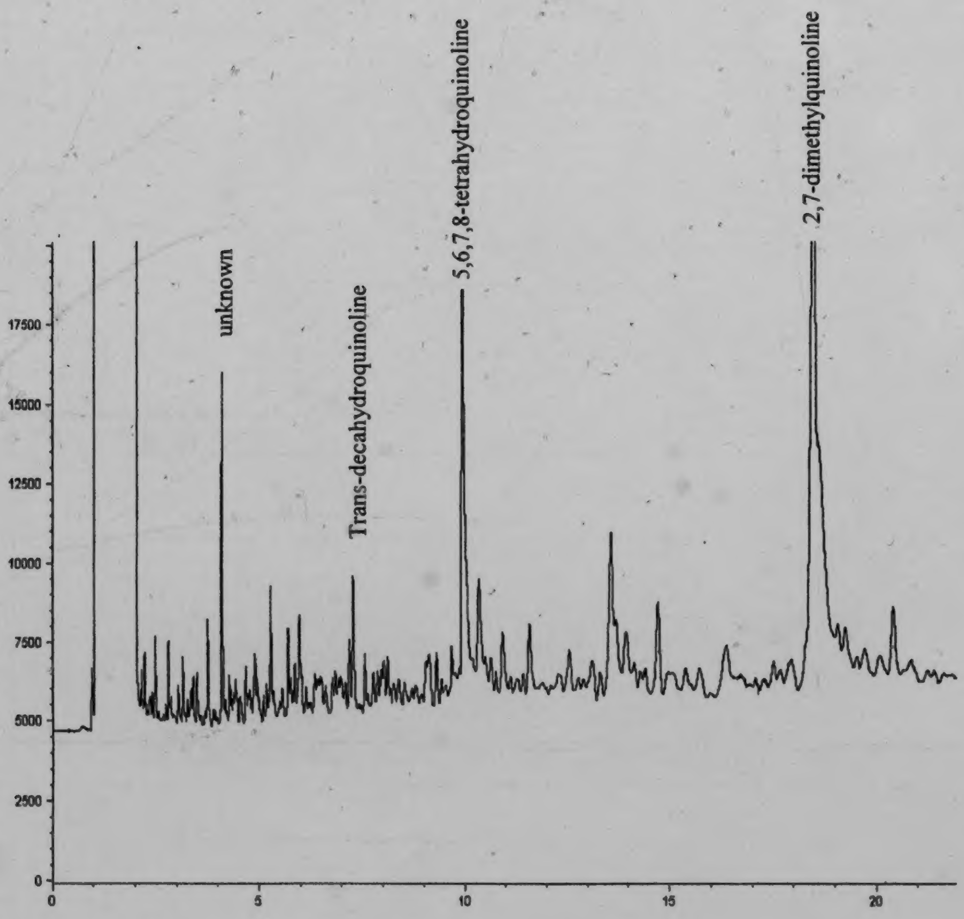

Figure B.3: GC Analysis of Decahydroquinoline Reaction with Cut 8

Appendix C

GC Calibration Curves

This appendix details the method and calculations used to determine the calibration curve constants during this work.

In order to calibrate the GC and determine the concentration of desired compound (usually quinoline) in a product oil sample, a calibration equation relating area ratios (AR) to mass ratios (MR) was required. The ratios were compound of interest (quinoline or decahydroquinoline) to internal standard (2,7-dimethylquinoline).

To determine the relationship between area and mass ratios, a number of calibration samples with known concentrations of desired compound in carrier oil were analyzed. The concentration of the desired compound in the calibration samples was controlled so that the entire range of calibration samples included the range of interest (post-reaction concentrations).

The calibration samples were prepared in the same way as the product oil samples. Approximately 0.2 g of the sample was placed in a 10 mL volumetric flask and the flask was then filled with methylene chloride. Then 4 mL of this 1st dilution was placed in a second 10 mL volumetric flask, the 2nd dilution. Internal standard (2,7-dimethylquinoline) was added to the 2nd dilution, as 3 mL from a 3.19×10^{-4} g/mL stock solution. The 2nd dilution volumetric flask was then filled with methlyene chloride. A portion of this final dilution was then fed to the GC.

After the calibration samples were analyzed by the GC, the resulting area ratios and mass ratios of the samples were fit to the following equation (Equation C.1) using linear regression, as performed by M.S. Excel. The constants Cal_{C1} and Cal_{C2} were determined.

$$MR = Cal_{C1} \times AR + Cal_{C2} \qquad \text{Equation C.1}$$

Since MR and AR were known in the calibration samples, the values of Cal_{C1} and Cal_{C2} are easily obtained. The relationship between MR and AR was always well represented by linear equations during this work.

During the analysis of a product oil sample where the concentration of the desired compound was unknown, the calibration equation could relate the area ratios returned by the GC to the actual mass ratios in the oil sample. The calculation method detailing the determination of product oil sample concentration is shown in another Appendix.

The calibration samples were typically made only from the desired compound and carrier gas oil. Addition of cuts was found to not interfere with the quinoline, decahydroquinoline, or 2,7-dimethylquinoline peaks and did not significantly interfere with the calibration equations.

An assumption that was made in order to use the calibration equation developed using unreacted carrier gas oil is that the carrier gas oil and cuts, once reacted, did not interfere with the GC integration or calibration.

A sample calibration equation development for quinoline is detailed below. Table C.1 shows the calibration sample and its dilution down to the 2nd dilution, as well as the internal standard dilution in order to determine the mass ratio (MR) being fed to the GC. Table C.2 shows the area ratio obtained by GC analysis for each of the mass ratios. Figure C.1 shows the MR and AR as well as the linear regression equation (Equation C.1) and the constants Cal$_{C1}$ and Cal$_{C2}$, which are 0.9911 and 0.0382 respectively.

Table C.1: Development of MR for Sample GC Calibration

Sample	Quinoline	To 1st Dilution	1st dilution Q concentration	2nd dilution Q concentration	2nd dilution DMQ concentration	Mass Ratio (MR) Q to DMQ
	(%)	(g)	(g/mL)	(g/mL)	(g/mL)	
1	1.0054	0.215	0.00021618	8.647E-05	9.57E-05	0.9036
2	0.6955	0.216	0.00015022	6.009E-05	9.57E-05	0.6279
3	0.6379	0.202	0.00012885	5.154E-05	9.57E-05	0.5386
4	0.4995	0.212	0.00010589	4.236E-05	9.57E-05	0.4426
5	0.3987	0.214	0.00008531	3.413E-05	9.57E-05	0.3566
6	0.2907	0.235	0.00006831	2.733E-05	9.57E-05	0.2855

Table C.2: Area Ratio and Mass Ratio for Sample GC Calibration

Sample	MR	Q Area	DMQ Area	AR
		(area counts)	(area counts)	
1	0.9036	219764	254067	0.8650
2	0.6279	163639	262921	0.6224
3	0.5386	125772	253748	0.4957
4	0.4426	101396	263357	0.3850
5	0.3566	83216	259536	0.3206
6	0.2855	69314	263596	0.2630

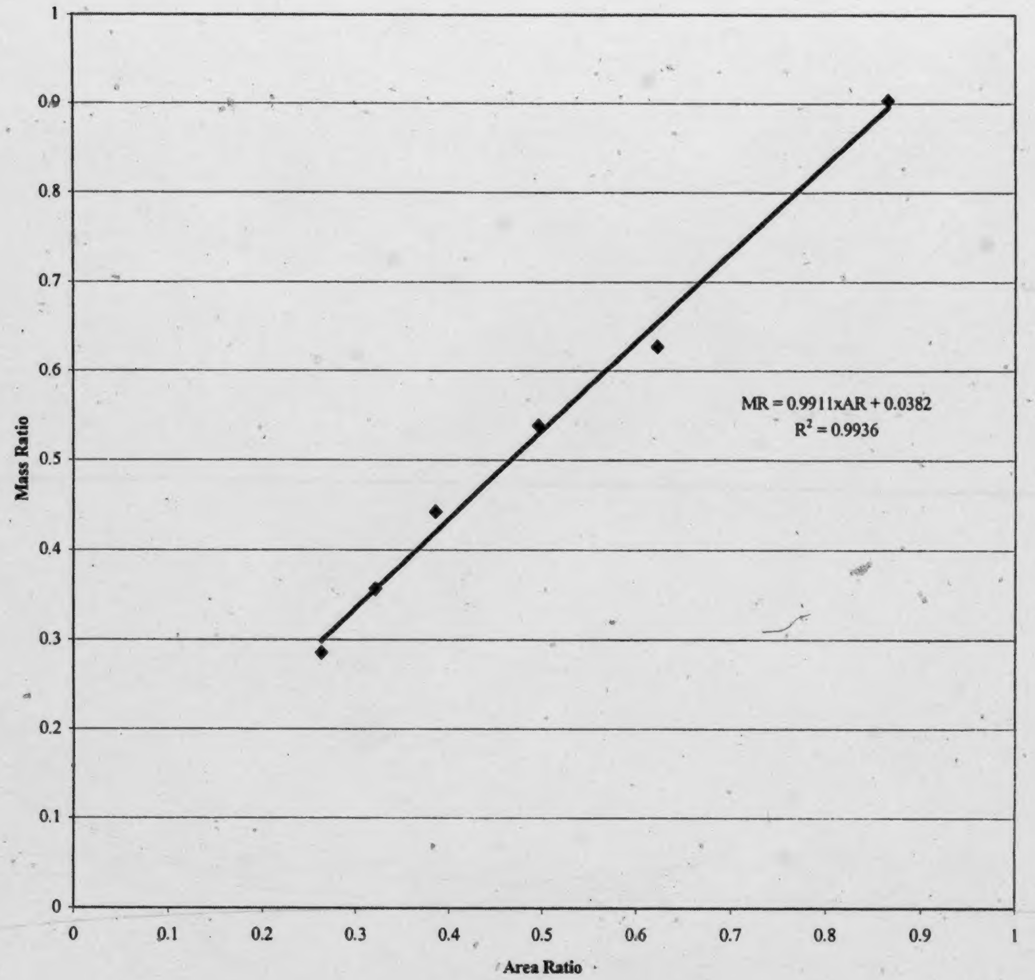

Figure C.1: Linear Regression of Calibration Samples

Appendix D

Reaction Kinetics

This appendix details the reaction kinetics and the calculations used to determine kinetic parameters and rate predictions during this work.

D.1 Development of Kinetic Rate Expression

The kinetics were assumed to behave in typical LHHW fashion and neglecting hydrogen adsorption and dissociation as well as internal and external diffusion of reactants and products around the catalyst, the following three 'reaction' expressions were determined.

Quinoline Adsorption $Q + S \xleftrightarrow{K'} QS$ Equation D.1

Quinoline Reaction $QS \xrightarrow{kr} S + P$ Equation D.2

Inhibition $I + S \xleftrightarrow{K'_I} IS$ Equation D.3

Where the term, S, is used to denote a catalyst 'site', Q is quinoline, P, is reaction products, and I is the inhibitory species. QS and IS represent catalyst sites that are occupied by the given component. The constants K' and K'_I are given in Equations D.4 and D.5, and the total number of sites on a catalyst, S_t, is shown in Equation D.6. The items in [] indicate the concentration of those items.

$$K' = \frac{[QS]}{[Q][S]} \qquad \text{Equation D.4}$$

$$K'_I = \frac{[IS]}{[I][S]} \qquad \text{Equation D.5}$$

$$S_t = [S] + [QS] + [IS] = S(1 + K'[Q] + K'_I\,[I]) \qquad \text{Equation D.6}$$

Assuming that the reaction rate equation is the rate limiting step, the rate of quinoline reaction is shown in Equation D.7.

$$rate = k_r[QS] = k_r K'[Q][S] = \frac{k_r K'[Q] S_t}{1 + K'[Q] + K'_I\,[I]} \qquad \text{Equation D.7}$$

Since the actual number of sites on a given catalyst was not determined, a reference value is considered. The activity of the catalyst, a, is a ratio of the number of sites on the given catalyst, S_t, to some reference value, S_o. In the kinetic analysis shown in Chapter 4, the catalyst sample used for determining the k and K values in Section 4.5 was considered to be the reference value, so the activity, a, had the value of unity. Subsequent catalyst samples then would have a non-unity activity relative to the reference sample. The rate equation is then expressed in Equation D.9.

$$a = \frac{S_t}{S_o} \qquad \text{Equation D.8}$$

$$rate = \frac{ak'[Q]}{1 + K'[Q] + K'_I\,[I]} \qquad \text{Equation D.9}$$

The rate expression developed in Equation D.9, is of the same format as developed by Giola and Lee (1986), Satterfield and Smith (1986), plus others.

For a constant volume batch reactor, the equation that represents the closed system is shown in Equation D.10, where w_{cat} is the weight of the catalyst, V_L is the volume of the liquid, and t is the time (in minutes).

$$rate = -V_L \frac{d[Q]}{dt} = \frac{w_{cat} a k'[Q]}{1 + K'[Q] + K'_I [I]} \qquad \text{Equation D.10}$$

The above equations are in terms of concentration of component (g/mL) for I and Q, but the work done used quinoline on a molar concentration basis (mol Q/g Feed), and the inhibitor concentration is a mass fraction ratio, so the density of the liquid feed and the molecular weight if the inhibitory fraction is factored in as shown in Equation D.11. The symbol 'C' is the molar concentration of quinoline, and 'I' is the mass fraction of the inhibitor.

$$rate = -V_L \rho_L \frac{dC}{dt} = \frac{w_{cat} a k' \rho_L C}{1 + K' \rho_L C + K'_I \rho_L MW_I I} \qquad \text{Equation D.11}$$

The rate expression is then simplified to account for all of the constants and is shown in Equation D.12.

$$rate = -\frac{dC}{dt} = \frac{a \frac{w_{cat}}{W_L} kC}{1 + KC + K_I I} \qquad \text{Equation D.12}$$

The ratio of catalyst weight to liquid weight was always held constant during this work, at a value of 1 to 25, so this constant was included in the value of k and Equation D.13 is seen, which is the same as Equation 4.7.

$$rate = -\frac{dC}{dt} = \frac{akC}{1 + KC + K_I I} \qquad \text{Equation D.13}$$

D.2 Determination of Kinetic Parameters

From Equation D.13, the kinetic parameters of k and K were determined from a series of clean feed reactions. The rate expression in Equation D.13 is integrated from 0 to t (the time of the reaction) and Equation D.14 results.

$$K(C_t - C_o) + (1 + K_I I)\ln(\frac{C_t}{C_o}) = -akt \qquad \text{Equation D.14}$$

Rearranging Equation D.14, Equation D.15 results, where the left hand side of the equation is equivalent to the average rate of reaction.

$$\frac{(C_o - C_t)}{t} = ak + \frac{(1 + K_I I)}{Kt}\ln(\frac{C_t}{C_o}) \qquad \text{Equation D.15}$$

For the series of clean feed reactions used to determine k and K, there were no inhibitors in the reaction (I=0). From the experiments, the values of C_t and C_o were known, along with t. The average reaction rate (left hand side of Equation D.15) was plotted against the natural log of C_t over C_0. MS Excel was then used to determine the slope and intercept of the plot and the value of k and K were then calculated to be $5.97\text{x}10^{-2}$ g feed^{1} g cat^{-1} min^{-1} and $1.08\text{x}10^{4}$ g feed^{1} mol Q^{-1} respectively. Once k and K were known, Equation D.13 was numerically integrated to predict final quinoline concentrations (and determine average reaction rates). The results of these predictions are shown in Figure 4.12 and Figure 4.13.

D.3 Development of Inhibition Kinetics

To determine the reaction kinetics of other catalyst batches, the activity, a, was determined from clean feed reactions with the catalyst batch in question. Equation D.13 was numerically integrated and the activity was determined in order to fit the values of C_t, C_o, t, with the same k and K values. The activity was determined for the catalyst by using the clean feed reactions following the inhibitor reactions (Cuts). Table D.1 shows the various parameters of Equation D.13 and the activity for the catalyst used in the Cut 4 3000 ppm total nitrogen study at 380 °C.

Table D.1: Sample Input/Output to Determine Catalyst Activity

Parameter	**Determined by**	**Value**
k	Previous kinetic analysis	$5.97\mathrm{x}10^{-2}$ g feed^{1} g cat^{-1} min^{-1}
K	Previous kinetic analysis	$1.08\mathrm{x}10^{4}$ g feed^{1} mol Q^{-1}
t	Experimental parameter	20 min
Q_o	Experimental parameter	$7.74\mathrm{x}10^{-5}$ mol Q^{1} g feed^{-1}
Q_t	Experimental result (measured)	$3.77\mathrm{x}10^{-5}$ mol Q^{1} g feed^{-1}
a	Determined (Numerical Integration)	0.945

For the reactions involving the inhibitory compounds (Cuts 2, 4, and 8) at 3000 ppm total nitrogen, Equation D.13 was numerically integrated again, and the value of K_I to fit the known values of k, K, a, C_t, C_o, I, and t was determined for Cut 2, Cut 4, and Cut 8. To determine the range of K_I, the numerical integration was completed over the range of C_t (upper and lower 95% confidence limits for each series of reactions with each Cut). Table D.2 shows the various values of the equation parameters for the 3000 ppm total nitrogen Cut 4 reactions.

Table D.2: Sample Input/Output to Determine Inhibition Constant

Parameter	Determined by	Value
k	Previous kinetic analysis	$5.97\text{x}10^{-2}$ g feed^1 g cat^{-1} min^{-1}
K	Previous kinetic analysis	$1.08\text{x}10^{4}$ g feed^1 mol Q^{-1}
t	Experimental parameter	20 min
I	Experimental parameter	0.456 g Cut 4^1 g feed^{-1}
C_o	Experimental parameter	$7.74\text{x}10^{-5}$ mol Q^1 g feed^{-1}
C_t	Experimental result (measured)	$5.03\text{x}10^{-5}$ mol Q^1 g feed^{-1}
C_t -upper	Experimental result (measured)	$4.82\text{x}10^{-5}$ mol Q^1 g feed^{-1}
C_t -lower	Experimental result (measured)	$5.23\text{x}10^{-5}$ mol Q^1 g feed^{-1}
a	Calculated Prior (Table D.1)	0.945
K_I	Determined (Numerical Integration)	2.14
K_I -upper	Determined (Numerical Integration)	2.71
K_I -lower	Determined (Numerical Integration)	1.66

To predict the 2000 ppm total nitrogen average reaction rates, Equation D.13 was numerically integrated again, with the values of k, K, a, C_o, t, and I in order to predict C_t. Table D.3 shows the prediction of the Cut 4, 2000 ppm total nitrogen reactions parameters. The upper and lower predictions of C_t are the result of the error or range of K_I as determined in Table D.2.

From the C_t and C_o values, the average reaction rate of quinoline can be determined by subtracting the two values and dividing by the time of the reaction. The above results are sometimes referred to by average reaction rate in the Results Chapter of this work.

Table D.3: Sample Prediction of Inhibition Effects on Quinoline Reaction

Parameter	**Determined by**	**Value**
k	Previous kinetic analysis	$5.97\text{x}10^{-2}$ g feed^{1} g cat^{-1} min^{-1}
K	Previous kinetic analysis	$1.08\text{x}10^{4}$ g feed^{1} mol Q^{-1}
t	Experimental parameter	20 min
I	Experimental parameter	0.228 g Cut 4^{1} g feed^{-1}
C_o	Experimental parameter	$7.74\text{x}10^{-5}$ mol Q^{1} g feed^{-1}
a	Calculated Prior (not shown)	1.18
K_I	Calculated Prior (Table D.2)	2.14
K_I -upper	Calculated Prior (Table D.2)	2.71
K_I -lower	Calculated Prior (Table D.2)	1.66
C_t	Prediction (Numerical Integration)	$3.89\text{x}10^{-5}$ mol Q^{1} g feed^{-1}
C_t -upper	Prediction (Numerical Integration)	$4.07\text{x}10^{-5}$ mol Q^{1} g feed^{-1}
C_t -lower	Prediction (Numerical Integration)	$3.73\text{x}10^{-5}$ mol Q^{1} g feed^{-1}
C_t -actual	Experimental result (measured)	$3.91\text{x}10^{-5}$ mol Q^{1} g feed^{-1}

Appendix E

Statistics – Student-t Distribution and Outlier Analysis

This appendix details the student-t distribution used to develop the 95 % confidence levels indicated in this work as well as the outlier analysis used.

E.1 Outlier Removal from Reaction Series

A number of replicate reactions were performed for each reaction series during this work. Since the reactions were performed in batch reactors, a series of several reactions would be performed. On occasion when one reaction in the series was considered suspect due to known experimental error (i.e. oil was noticed leaking from the reactor during reaction), it was removed from the series during calculation. All other points were used during the statistical analysis of the reaction series, except for those points that could be shown to be outliers statistically as defined in Scheaffer and McClave (1995). Outliers are those points that are 1.5 inter-quartile ranges lower than the 1st quartile or 1.5 inter-quartile ranges more than the 3rd quartile.

MS Excel was used to determine the 1st and 3rd quartiles for each series of reactions. The difference between the 1st and 3rd quartiles is the inter-quartile range. Any points above or below 1.5 times the inter-quartile range away from the 1st or 3rd quartile was removed from the analysis. Table E.1 details one such analysis for a clean feed reaction, where all values are expressed in % conversion of quinoline. One point was removed during this particular analysis (data point of 63.9 % quinoline conversion).

Table E.1: Outlier Removal from Reaction Series Data

Data	Average	1st Quartile	3rd Quartile	2 inter-quartile ranges	Upper Limit	Lower Limit	Data Removed
63.9	51.7	48.1	54.2	6.1	63.4	39.0	63.9
52.2							
47.6							
48.3							
55.6							
53.7							
49.0							
43.1							

E.2 Development of 95 % Confidence Limits – Quinoline Conversion

The 95 % confidence limits shown during the Results Chapter on the quinoline conversion were determined using the student-t distribution as shown by Spiegel (1972). The equation for the 95 % confidence interval is shown in Equation E.1, where $t_{0.975}$ is the 95 % confidence co-efficient, σ is the standard deviation of the reaction series, and n is the number of samples in the series.

$$L = \frac{t_{0.975} x \sigma}{\sqrt{n-1}} \qquad \text{Equation E.1}$$

The value of $t_{0.975}$ depends on the number of samples in the series (n). Table E.2 shows the $t_{0.975}$ values for the given n. The 95 % confidence value for a given reaction series is the experimental average of the series plus or minus the 95 %

confidence interval (L). For a series of reactions then, it can be said that with 95 % confidence, the actual average for that reaction series is within the range given by Equation E.2, where $\overline{X}$ is the experimental average.

$$Range = \overline{X} \pm L \qquad \text{Equation E.2}$$

Table E.2: 95 % Confidence Co-efficient as a Function of number of samples

n	**$t_{0.975}$**
4	3.18
5	2.78
6	2.57
7	2.45
8	2.36
9	2.31
10	2.26
11	2.23
12	2.20
13	2.18
14	2.16
15	2.14
16	2.13

Appendix F

Methylene Chloride in Cut 8 CH_2Cl_2 Extract

This appendix shows the NMR results performed on the Cut 8 Methylene Chloride nitrogen extract. During reactions with this extract, the reactor walls became 'activated' and the catalyst was damaged severely. The catalyst activity dropped significantly while the apparent reaction increased due to the very high catalytic activity of the reactor walls.

The suspected cause of these unusual results was chlorine damage to the catalyst and reactor walls due to methylene chloride contamination of the Cut 8 extract. Figure F.1 shows the results of the NMR analysis performed by the Department of Chemistry at the University of Alberta. Deuterated chloroform was used as the solvent in the NMR analysis. The analysis shows that 1 out of every 148 hydrogen atoms was from methlyene chloride. From the Cut 8 extract data, the total content of hydrogen atoms in the cut was 8.2 wt %. Combining this information yields that the Cut 8 extract was found to have 23300 ppm methlyene chloride in the extract. Equation F.1 and F.2 details the calculation and the result. In the equations, all the values are in mass ratios of grams of item of interest per gram of another item. For example, there is 84.9 g of Methylene Chloride for every 2.02 g of Hydrogen in Methylene Chloride.

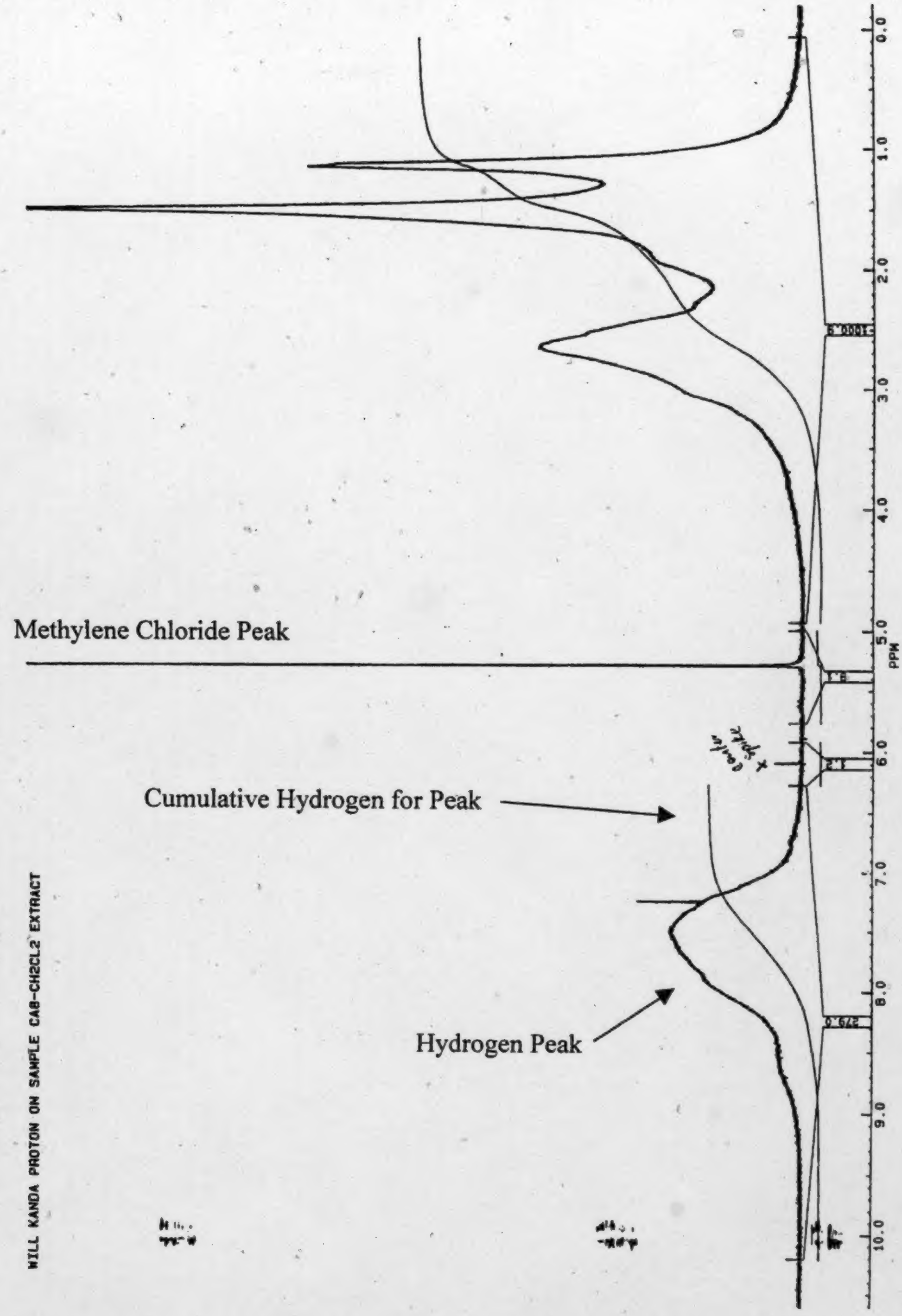

Figure F.1: NMR Analysis of Cut 8 Methylene Chloride Extract

$$CH_2Cl_2(wtfrac) = 0.082\frac{gH}{gextract}x\frac{1}{148}\frac{gHinCH_2Cl_2}{gH}x\frac{84.9}{2.02}\frac{gCH_2Cl_2}{gHinCH_2Cl_2}=0.0233$$

Equation F.1

$$CH_2Cl_2(ppm) = 0.0233x1000000 = 23300$$

Equation F.2